

ELECTRONIC AND OPTICAL PROPERTIES OF EXAMPLE 2D SYSTEMS UNDER THE VERTICAL ELECTRIC FIELD

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By
Yılmaz Can Yüksek
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We certify that we have read this thesis and that in our opinion it is fully adequate,
in scope and in quality, as a thesis for the degree of Master of Science.

Oğuz Gülseren(Advisor)

Bekir Sıtkı Kandemir

Ceyhun Bulutay

Approved for the Graduate School of Engineering and Science:

Orhan Arıkan
Director of the Graduate School

ABSTRACT

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Yılmaz Can Yüksek

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Advisor: Oğuz Gülseren

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From optics to nanoelectronics, two-dimensional (2D) materials have drawn attention due to their extraordinary properties such as high carrier mobility, good thermal and electrical conductivity, and mechanical strength. Electronic and optical properties of example 2D systems containing single-layer graphene, 2D molybdenum carbide (Mo_2C), and 2D tungsten diselenide (WSe_2) under the vertical (perpendicular) static electric field (E-field) varying between 0.1 V/Å and 2.5 V/Å are investigated by the first principles calculations based on the density functional theory. Contributions of van der Waals interactions are included by selecting a suitable exchange-correlation functional. Electronic band structure and density of states information confirmed that monolayer graphene and single-layer Mo_2C exhibit metallic properties whereas 2D WSe_2 is a semiconductor with a direct band gap. For all systems up to some magnitude of the E-field, the bands in the valence band were found to be degenerate whereas shifts took place in the conduction band as the E-field was introduced to the system. By increasing E-field amplitudes, the Dirac point shifted upwards in graphene, and σ^* band shifted below the Fermi level at 0.5 V/Å. In addition to four well-known interband transitions ($\pi \rightarrow \pi^*$, $\sigma \rightarrow \sigma^*$, $\sigma \rightarrow \pi^*$, $\pi \rightarrow \sigma^*$), $\sigma^* \rightarrow \pi^*$ transition is observed. After an electric field amplitude (E_z) of 0.8 V/Å, bands due to the s-orbitals of Mo atoms in monolayer Mo_2C shifted below the Fermi level. Additionally, π plasmon peaks redshifted up to 0.4 V/Å and blueshifted for $0.6 \text{ V/Å} \leq E_z \leq 2.5 \text{ V/Å}$. For the monolayer WSe_2 system, the band gap becomes zero when $E_z \geq 1.0 \text{ V/Å}$ which indicates a semiconductor-to-metal transition under the E-field. Shifts below the Fermi level enabled us to n-dope those systems.

Keywords: Vertical (perpendicular) static electric field, graphene, 2D Mo_2C , 2D

WSe_2 , electronic and optical properties, interband transitions, doping, density functional theory.



ÖZET

ELEKTRİK ALAN ALTINDA ÖRNEK İKİ BOYUTLU SİSTEMLERİN ELEKTRONİK VE OPTİK ÖZELLİKLERİ

Yılmaz Can Yüksek

Fizik, Yüksek Lisans

Tez Danışmanı: Oğuz Gülseren

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Yüksek taşıyıcı hareket kabiliyeti, üstün termal ve elektriksel iletkenlik ve mekanik sağlamlığı kapsayan olağanüstü özelliklerinden dolayı iki-boyutlu (2B) malzemeler optikten nanoelektronığe kadar çeşitli alanlarda kullanılmaktadır. Bu tez çalışmasında tek katmanlı grafen, 2B molübden karbür (Mo_2C) ve 2B tungsten diselenidi (WSe_2) kapsayan örnek 2B sistemlerin 0.1 V/Å ve 2.5 V/Å arasında uygulanan dikey statik elektrik alan (E-alan) altındaki elektronik ve optik özellikleri yoğunluk fonksiyonel teorisine dayanan ilk prensip hesaplamalar ile araştırılmıştır. Uygun değiş-tokuş fonksiyoneli kullanılarak van der Waals etkileşimleri hesaplara dahil edildi. Elektronik bant diyagramları ve durum yoğunluğu grafikleri kullanılarak tek katmanlı grafen ve 2B Mo_2C sistemlerinin metal, direkt bant aralığına sahip 2B WSe_2 sisteminin ise yarıiletken özellikler gösterdiği doğrulanmıştır. E-alan altında araştırılan sistemlerin tamamında değerlik bandındaki bantların belirli bir E-alan genliğine (E_z) kadar eş enerjili olduğu gözlenirken iletim bandında ise E-alan uygulandığı an kaymalar gözlenmiştir. Grafende artan elektrik alan etkisiyle Dirac noktası yukarı kaymaya, $E_z = 0.5 \text{ V/Å}$ iken σ^* bandı ise Fermi seviyesinin (E_F) altına kaymaya başlamıştır. Grafen için bilinen bant geçişlerine ($\pi \rightarrow \pi^*$, $\sigma \rightarrow \sigma^*$, $\sigma \rightarrow \pi^*$, $\pi \rightarrow \sigma^*$) ek olarak, $\sigma^* \rightarrow \pi^*$ geçişi gözlenmiştir. 2B Mo_2C için $E_z > 0.8 \text{ V/Å}$ olduğunda Mo atomlarına ait s-orbitallerine karşılık gelen bantlar E_F altına kaymış, ve π plazmon tepelerinin $E_z \leq 0.4 \text{ V/Å}$ için kırmızıya, $0.6 \text{ V/Å} \leq E_z \leq 2.5 \text{ V/Å}$ için ise maviye kaydığı görülmüştür. $E_z \geq 1.0 \text{ V/Å}$ olduğunda 2B WSe_2 sisteminin bant aralığı sıfır olarak elde edildiğinden yarıiletkenden metale geçiş gözlemlendi. E_F altına kaymalar çalışılan malzemelerin n-katkılamasını sağladı.

Anahtar sözcükler: Dikey statik elektrik alan, grafen, 2B Mo_2C , 2B WSe_2 , elektronik ve optik özellikler, bant geçişleri, katkılama, yoğunluk fonksiyonel teorisi.

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Chapter 1

Introduction

In the last couple of decades, two-dimensional (2D) materials have significantly drawn attention and are frequently used in electronics, optics, and optoelectronics due to their extraordinary properties such as thermal conductivity, mechanical strength, and high carrier mobility[8, 9, 10, 11, 12]. Experimentally, it is possible to synthesize small and large-area monolayers with high-quality by using techniques involving chemical vapor deposition (CVD) [13, 14, 15, 16, 17, 18] and physical vapor deposition (PVD) [19, 20, 21].

Semiconducting and insulating materials have band gaps whereas metals do not since their valence and conduction bands overlap [22]. They both have different application areas. For instance, for metallic materials, not having a band gap implies the electrons to conduct electricity due to their free motion within the metals whereas it might limit its usage in nanoelectronics. However, in the application area of field-effect transistors, semiconductors either in 2D or bulk forms are utilized as channels between the source and drain since they have a wide band gap and are proper to control the current status on and off [23, 24]. Even though monolayer graphene exhibits extraordinary properties as cited above, there is a drawback to use this excellent material: not having a band gap. As Fig. 1.3 displays the energy band diagram and local density of states (DOS) for monolayer graphene obtained by calculations from first principles based on the

density functional theory, single-layer graphene does not have a band gap. To tune electronic and optical properties of materials, one may apply electric field [25, 26, 27, 28, 29, 30] or mechanical strain to the system [31, 32, 33]. In addition to the last two cited methods, band gap engineering is possible by forming van der Waals heterostructures which are forming heterostructures by stacking different 2D materials on top of each other, doping, and varying the number of layers of the system which allows adjusting the width of band gap with external effects [28, 29, 30, 34, 35, 36, 37].

The Fermi energy (E_F) is the highest occupied level of the electrons in the ground state of a system [22]. By applying an external electric field, the Fermi level will be shifted due to the transfer of electrons from occupied to unoccupied states [38]. An example to such a circumstance is the working principle of the scanning tunneling microscope (STM) which is based on the quantum tunneling between the tip and the surface of the material that the tip is scanning through. As the tip of STM scans the surface of the sample, in the presence of an external bias, a tunneling current occurs which allows electrons to tunnel through the vacuum between tip and sample [39]. Therefore, the Fermi level becomes shifted in the presence of the bias so that the electrons are transferred from occupied states towards the unoccupied ones [40].

This thesis contains the following: In Chapter 1, general features of investigated metallic and semiconducting monolayers are explained in a nutshell which are graphene and Mo_2C being metals, and WSe_2 being a semiconductor. Details on the theoretical background are provided in Chapter 2. Electrical and optical properties of above-cited materials are studied in Chapter 3 corresponding to the monolayer graphene, Chapter 4 for 2D Mo_2C , and those corresponding to single-layer WSe_2 are included in Chapter 5. Eventually, conclusions about the whole thesis are provided in Chapter 6.

1.1 Monolayer Graphene

By its energy band dispersion relation, graphene is a novel 2D, one atom thick, sp^2 hybridized material that is formed by carbon (C) atoms organized in a triangular lattice with an interatomic distance of 1.42 Å. Some of the properties that make graphene a significantly preferable and widely used monolayer are high carrier mobility, thermal conductivity, and mechanical strength [8, 9, 10, 41]. The primitive unit cell of monolayer graphene consists of two nonequivalent carbon atoms as shown in Fig. 1.1a. In Fig. 1.1b and Fig. 1.1c, top view and the general structure of the monolayer graphene sheet are indicated, respectively. In this thesis, all of the figures corresponding to the structure of the materials are obtained using VESTA [42].

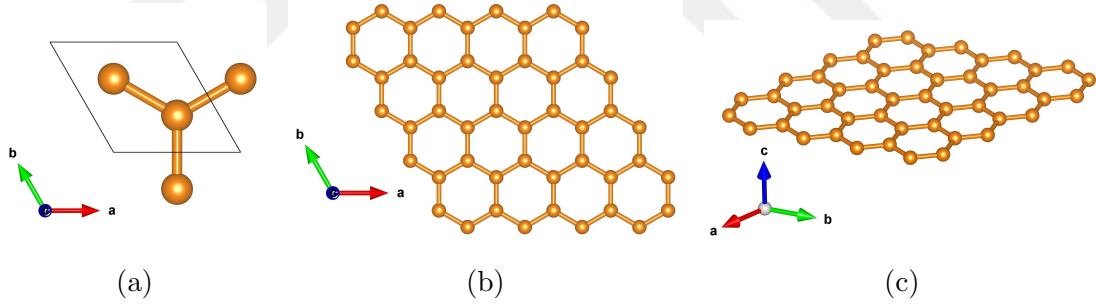


Figure 1.1: For monolayer graphene: (a) Primitive unit cell. (b) View from the top. (c) General structure. In the coordinate system shown above a , b , and c axes represent x , y , and z axes, respectively. Orange atoms represent C atoms.

A crystal lattice is described by the lattice translation vectors [22]. Primitive lattice vectors $\vec{a}_i$ with $i = 1, 2$ and reciprocal lattice vectors $\vec{b}_j$ with $j = 1, 2$ corresponding to monolayer graphene are given in Equations 1.1, and 1.2, respectively. In Fig. 1.2, the lattice vectors in direct and reciprocal lattices are shown.

$$\vec{a}_1 = \frac{3a}{2}\hat{x} + \frac{a\sqrt{3}}{2}\hat{y}, \quad \vec{a}_2 = \frac{3a}{2}\hat{x} - \frac{a\sqrt{3}}{2}\hat{y} \quad (1.1)$$

$$\vec{b}_1 = \frac{2\pi}{3a}(\hat{x} + \sqrt{3}\hat{y}), \quad \vec{b}_2 = \frac{2\pi}{3a}(\hat{x} - \sqrt{3}\hat{y}). \quad (1.2)$$

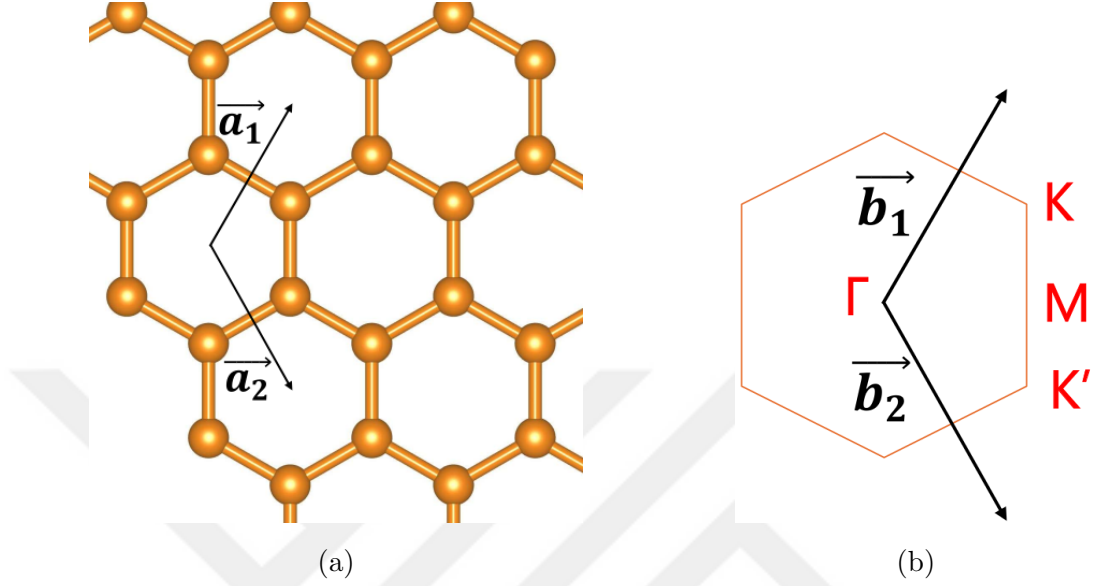


Figure 1.2: Corresponding to the monolayer graphene: (a) Direct lattice and lattice translation vectors $\vec{a}_1$ and $\vec{a}_2$. (b) First Brillouin zone and corresponding vectors $\vec{b}_1$, $\vec{b}_2$, and high symmetry points in the first Brillouin zone.

In 1947, linear dispersion of monolayer graphene was first theoretically described by P. R. Wallace. As mentioned previously, the crystal structure of graphene is honeycomb structure with a hexagonal Brillouin zone (BZ). E_F passes through the K and K' points in the first BZ, called the Dirac points, corresponding to a linear dispersion relation and they form the Dirac cone. At the Fermi level, six Dirac points coincide which are single points that connect the conduction band (CB) and valance band (VB) [43]. In the condensed matter world, Schrödinger equation is sufficient for describing non-relativistic particles. However, since the charge carriers in graphene effectively behave as relativistic particles, called massless Dirac fermions, as were described by Dirac equation [41]. Dirac points are found to be located in the positions classified in Equation 1.3 in momentum space [44].

$$\vec{K} = \frac{2}{3} \left(\frac{\pi}{a} \hat{x} + \frac{\pi}{a\sqrt{3}} \hat{y} \right), \quad \vec{K}' = \frac{2}{3} \left(\frac{\pi}{a} \hat{x} - \frac{\pi}{a\sqrt{3}} \hat{y} \right) \quad (1.3)$$

In Fig. 1.3 electronic band structure and DOS plot of single-layer graphene as well as possible interband transitions are provided by the density functional theory (DFT). As indicated, a band gap is not present in the single-layer graphene which results in zero DOS at E_F . In 1953, van Hove singularity was observed by L. van Hove via the phonon spectrum of a crystal as a non-differentiable point [45]. The results of L. van Hove were in accordance with the DOS calculations corresponding to the two-dimensional graphite layer in [46] as well, which are van Hove singularities in the DOS of monolayer graphene. Van Hove singularities may have beneficial features for the electronic and optical properties of the materials [47]. For instance, van Hove singularity in DOS appears as a sharp peak. As the peak gets sharper, electrons have more available states to fill in. Van Hove singularities can be seen in the DOS data obtained in Fig. 1.3 around -2.5 eV and 1.5 eV.

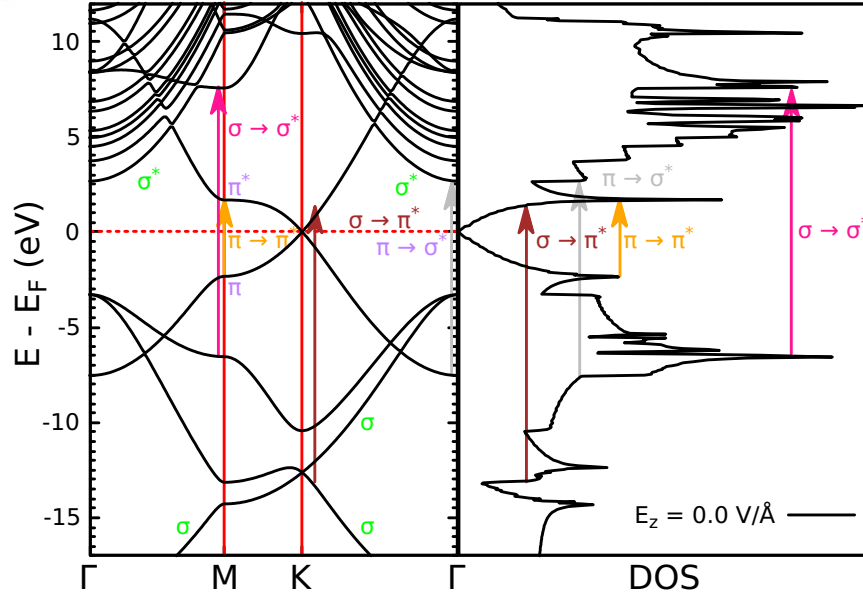


Figure 1.3: Energy band diagram, DOS plot, and interband transitions of monolayer graphene. E_F is shifted to zero.

Possible interband transitions as a result of optical transitions corresponding to single-layer graphene are provided in Fig. 1.3. Both in electronic band structure and DOS graphs, transitions are determined such that $\pi \rightarrow \pi^*$ transition is indicated with orange arrow, $\sigma \rightarrow \sigma^*$ transition is indicated with pink arrow, $\sigma \rightarrow \pi^*$ transition is indicated with brown arrow, and $\pi \rightarrow \sigma^*$ transition is indicated with gray arrow. It is worth considering that π bonds correspond to the p_z orbitals and are aligned orthogonal to the sp^2 orbitals. Along the graphene sheet, sp^2 orbitals are present which are corresponding to $2s$ orbital, and two p orbitals such that $2p_x$ and $2p_y$ [41]. For each C atom in graphene, one electron contribution is present due to the p_z orbital which allows this material to exhibit extraordinary (electronic) properties [48]. The imaginary part of the dielectric function is utilized to investigate the interconnection between light with material. Therefore, to obtain interband transition information, optical calculations can be utilized. Real and imaginary parts of dielectric function are denoted by $\varepsilon_1(\omega)$ and $\varepsilon_2(\omega)$, respectively, ω being the frequency of the electromagnetic wave. For the real part of the dielectric function, $\varepsilon_1^\perp$ refers to the perpendicular direction of polarization of light (along the z-axis) whereas $\varepsilon_1^\parallel$ represents the polarization in the planar direction. Similarly, for the imaginary part of the dielectric function, $\varepsilon_2^\perp$ refers to the perpendicular direction of polarization whereas $\varepsilon_2^\parallel$ represents the polarization in the planar direction, i.e., along the graphene sheet. $\varepsilon_2^\perp$ plots are used to identify $\pi \rightarrow \sigma^*$ and $\sigma \rightarrow \pi^*$ transitions whereas $\varepsilon_2^\parallel$ data indicate $\pi \rightarrow \pi^*$ and $\sigma \rightarrow \sigma^*$ transitions as studied in [49] and [50]. Those transitions are investigated intricately in Chapter 3.2 under the perpendicular static electric field.

1.2 Monolayer Molybdenum Carbide

Since it does not have a band gap as shown in Fig. 4.1 that is obtained by DFT, single-layer Mo_2C is another metal that has various application areas due to its significant properties. Additionally, it is thermally stable and can be produced via CVD with large-area and high-quality [17, 18]. Moreover, in low-temperature physics, 2D Mo_2C shows superconducting features which makes it a promising

substance. By ab initio calculations based on DFT, J. Lei et al. forecast that the most stable phase of 2D Mo_2C for superconductivity at low temperatures is 2H phase [51]. J. J. Zhang et al. confirmed the low-temperature superconductivity of monolayer molybdenum carbide by making use of DFT as well. Moreover, they also investigated the effect of functionalization of 2D Mo_2C on the superconductivity and found that bromine functionalized single-layer molybdenum carbide is a promising 2D superconductor [52]. Due to their high electrical conductivity similar to graphene, 2D Mo_2C may be utilized as a transparent conductive electrode for manufacturing sensors as well [53, 54].

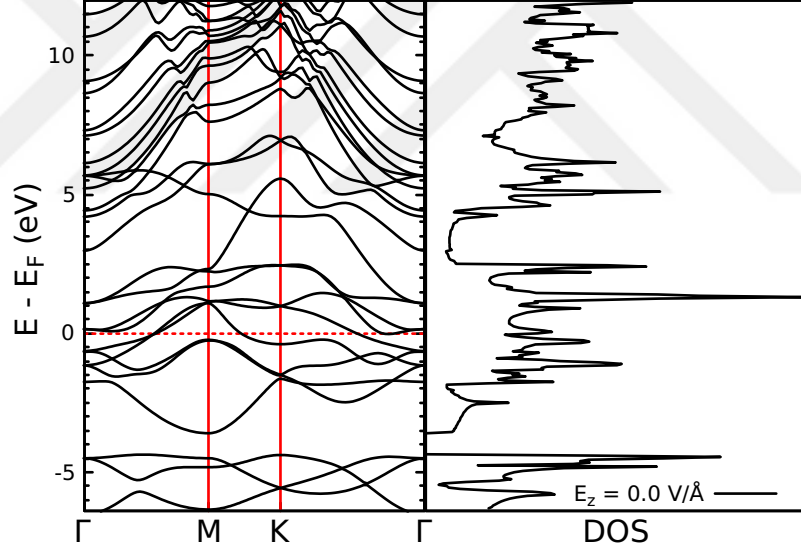


Figure 1.4: Electronic band diagram and DOS of 2D Mo_2C . E_F is set to zero.

The primitive unit cell of monolayer Mo_2C consists of two molybdenum (Mo) atoms and one C atom as shown in Fig. 1.5a and Fig. 1.5b. In Fig. 1.5c and Fig. 1.5d, the general structure and top view of a 4x4x1 monolayer Mo_2C supercell are shown, respectively.

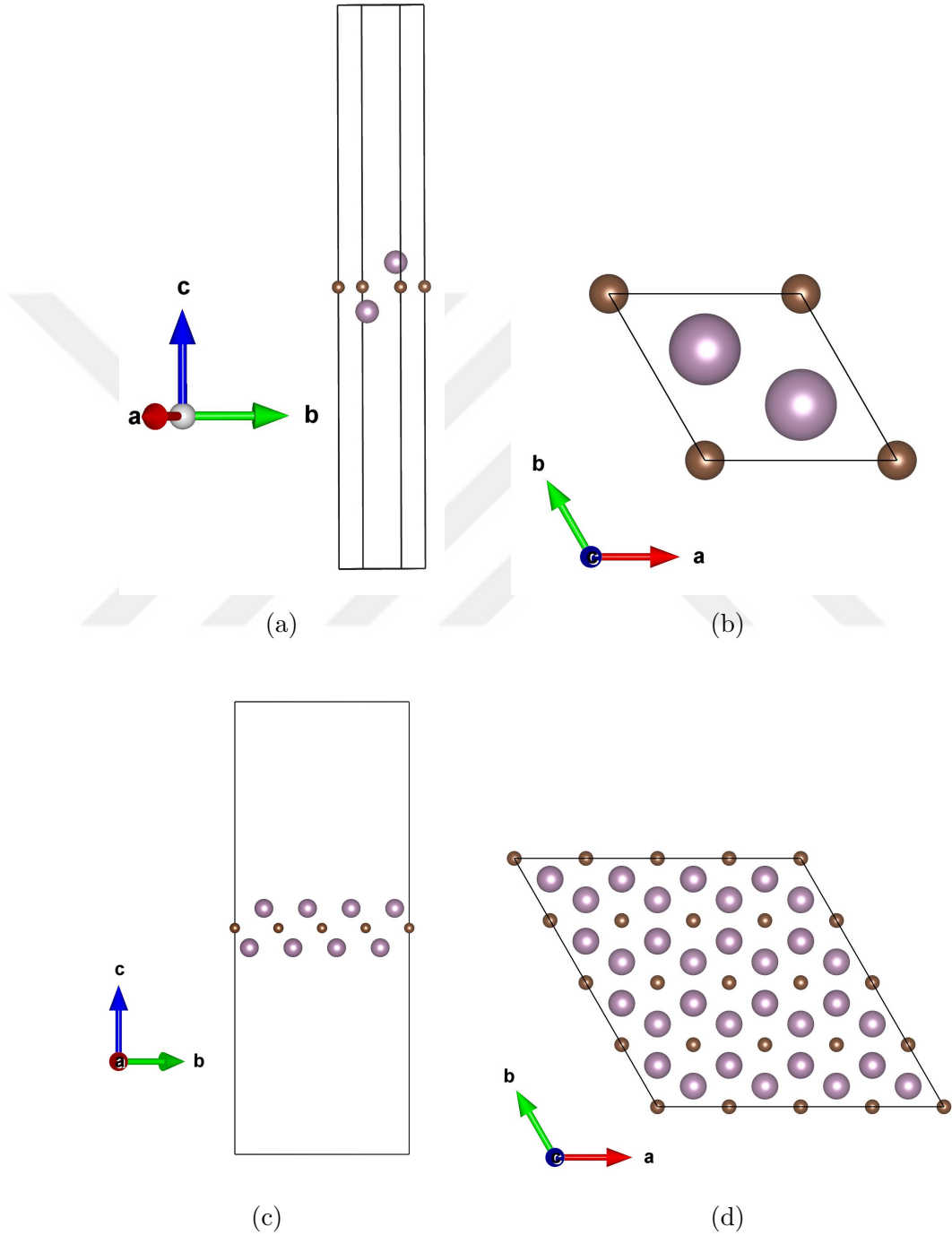


Figure 1.5: For 2D molybdenum carbide: (a) General view of the primitive unit cell. (b) Top view of the primitive unit cell. (c) View from the x-axis corresponding to $4 \times 4 \times 1$ supercell. (d) Top view of $4 \times 4 \times 1$ supercell. Purple atoms represent Mo whereas brown atoms stand for C. In the coordinate system indicated, a, b , and c axes represent x, y , and z axes, respectively.

1.3 Monolayer Tungsten Diselenide

Unlike the metallic systems mentioned in Sections 1.1 and 1.2, the third system investigated in this thesis is 2D hexagonal WSe_2 which is a semiconducting material having a direct band gap in the absence of any external effects. Using quantum mechanical calculations based on DFT as usual throughout this thesis, electronic band structure and DOS plots are obtained and given in Fig. 1.6 with a direct band gap of 1.60 eV at K point in the first BZ. Computational details for all of the calculations are explained in the corresponding chapters for each three considered materials. Experimentally, the structural parameter of 2D hexagonal tungsten diselenide is determined as 3.286 Å [3].

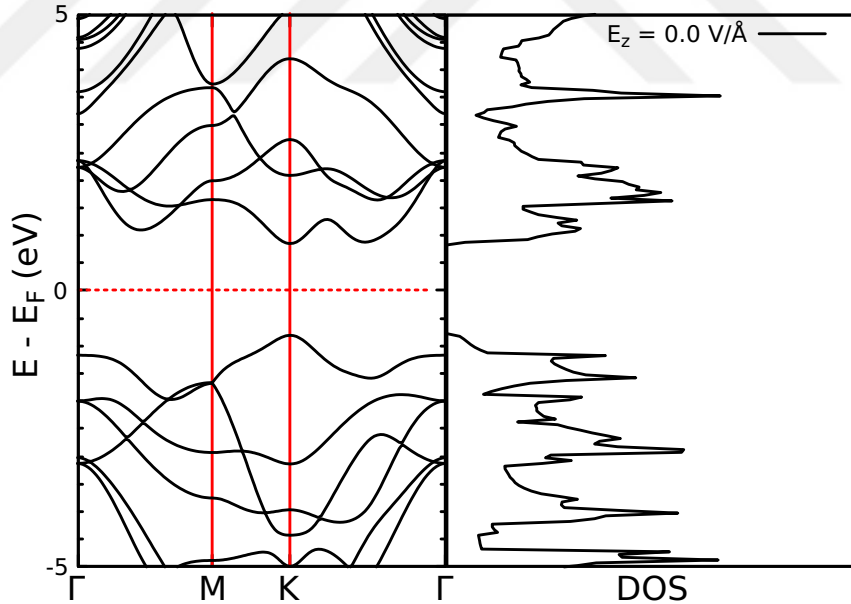


Figure 1.6: Energy band diagram and DOS plot of monolayer tungsten diselenide. E_F is shifted to zero.

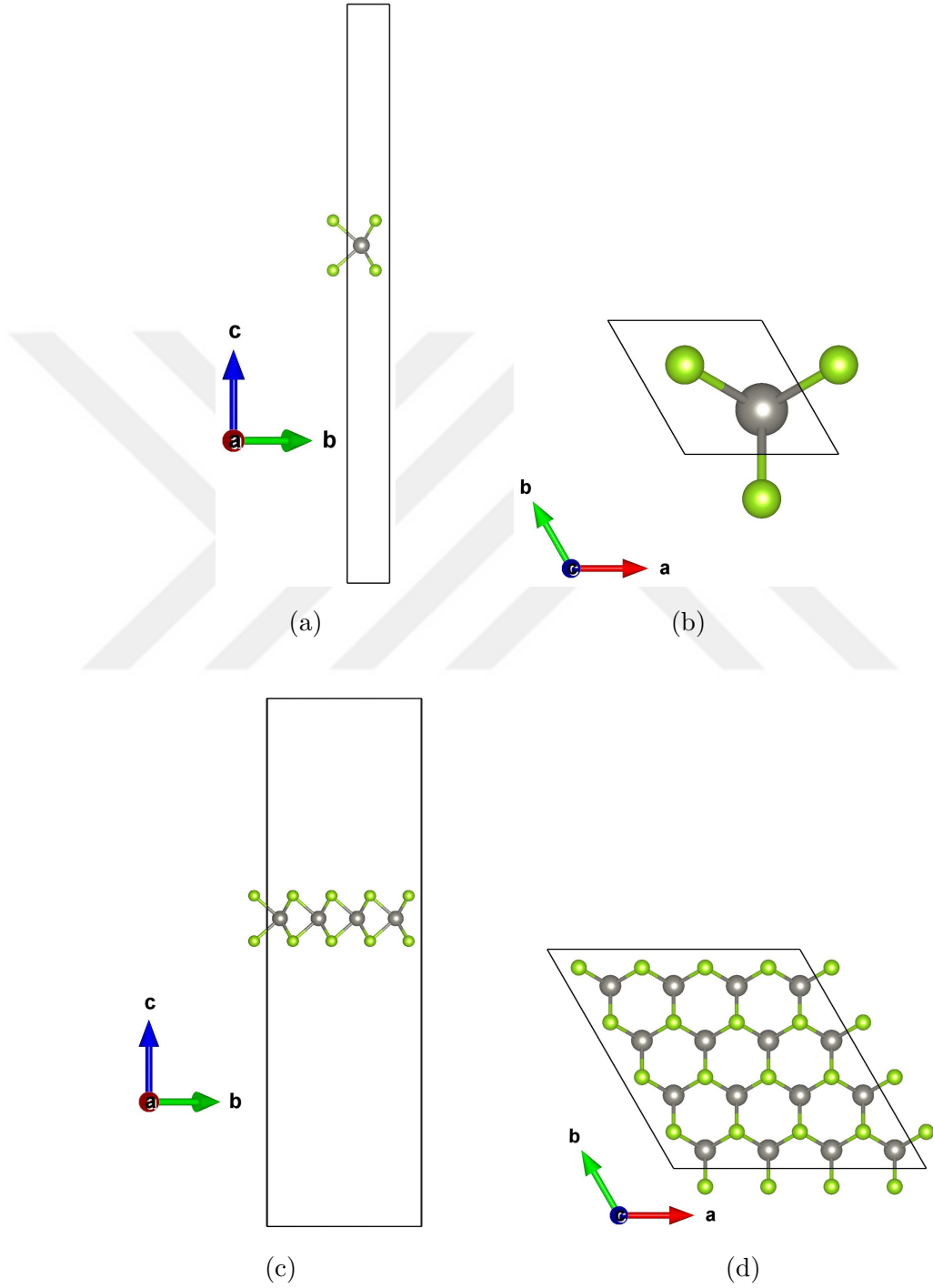


Figure 1.7: For 2D WSe_2 : (a) Side view of the primitive unit cell. (b) Top view of the primitive unit cell. (c) Side view corresponding to $4 \times 4 \times 1$ supercell. (d) Top view of the supercell. Gray atoms represent tungsten atoms whereas green atoms stand for selenium. In the coordinate system indicated, a , b , and c axes represent x , y , and z axes, respectively.

One of the application areas that semiconductors are mainly used is the field-effect transistor industry since semiconductors have band gap and high on/off ratio corresponding to the current [23, 55, 56, 57]. In electronics, WSe_2 is utilized since it has high carrier mobility [11, 12, 56] and powerful features for photoluminescence [58]. 2D WSe_2 is a thermally stable material [57] and can be synthesized using CVD [16]. As can be seen in Fig. 1.7, the primitive unit cell of monolayer WSe_2 contains one tungsten and two selenium atoms. Side and top views corresponding to its primitive unit cell and a 4x4x1 supercell are provided.

Chapter 2

Theoretical Background

To obtain material properties such as electronic properties, one should make use of either the Schrödinger equation or the Dirac equation. However, solving those equations gets extremely complicated as the number of electrons, N , in the system increases. Moreover, obtaining the exact solution to the Schrödinger equation becomes impossible as the system is getting complicated. It is even not easy to solve the Schrödinger equation corresponding to the water molecule since that system has 10 electrons and three nuclei in total. Therefore, to investigate the electronic properties of materials, solids, and molecules, a need for a new theory to approximate the solution of the Schrödinger equation arose. During the initial stages of the foundation of quantum mechanics, L. Thomas and E. Fermi introduced the Thomas-Fermi Theory in which they considered calculating the electron density ($n(\mathbf{r})$) where $\mathbf{r}$ corresponding to three spatial coordinates) rather than the wave functions. However, their theory did not work for diatomic systems [59]. In the mid-twentieth century, two articles that were the milestones for the density functional theory (DFT) were the work of P. Hohenberg and W. Kohn [60] published in 1964, and the next year the article published by W. Kohn and L. J. Sham [61]. As introduced in the Thomas-Fermi theory, DFT makes use of $n(\mathbf{r})$ instead of dealing with the many-body wave function [60, 62].

In physics, materials science, and computational chemistry, DFT is utilized to investigate the electronic properties of materials such as solids by using quantum mechanics. The fact that performing calculations by DTF is computationally affordable, makes DFT a frequently used theory in solid-state physics and other related branches of science. It is an accurate ab initio method when used suitably and is powerful for approximating the electronic charge density [63]. Ab initio calculations performed throughout the thesis have been implemented based on DFT.

2.1 Many-Body Schrödinger Equation

Based on the foundations of wave mechanics, the Schrödinger equation describes the wave function as time evolves. Completely non-relativistic time-dependent and time-independent Schrödinger equations without spin coordinate are provided in Equations 2.1 and 2.2, respectively.

$$i\hbar \frac{\partial \Psi(\mathbf{r}, t)}{\partial t} = \hat{H} \Psi(\mathbf{r}, t) \quad (2.1)$$

$$\hat{H} \psi(\mathbf{r}) = E \psi(\mathbf{r}) \quad (2.2)$$

where $\hat{H}$ is the Hamiltonian operator that contains kinetic and potential energy terms, Ψ is the wave function that depends on spatial and time variables, $\psi(\mathbf{r})$ is the wave function (eigenvector) with only spatial coordinate dependence, and E is the energy eigenvalue. There is a possible simplification for the Hamiltonian operator, that is the Born-Oppenheimer approximation which relies on the fact that the mass of nucleus m_M is quite heavier than the mass of electrons m_e . Therefore, due to its huge mass compared to that corresponding to electrons, it can be separated by frozen compared to the ions due to the fast electron motion [64].

By using the Born-Oppenheimer approximation, for N electrons and L nuclei, with electronic charge e and nuclear charge Z_I , the completely non-relativistic Hamiltonian is expressed as:

$$\begin{aligned} \hat{H} = & -\frac{\hbar^2}{2m_e} \sum_i^N \nabla_i^2 + \frac{1}{2} \frac{e^2}{4\pi\epsilon_0} \sum_i^N \sum_{i \neq j}^N \frac{1}{|\mathbf{r}_i - \mathbf{r}_j|} - \frac{e^2}{4\pi\epsilon_0} \sum_i^N \sum_I^L \frac{Z_I}{|\mathbf{r}_i - \mathbf{R}_I|} \\ & + \frac{1}{2} \frac{1}{4\pi\epsilon_0} \sum_I^L \sum_{I \neq J}^L e^2 \frac{Z_I Z_J}{|\mathbf{R}_I - \mathbf{R}_J|} \end{aligned} \quad (2.3)$$

In Eq. 2.3, indices corresponding to the electrons are i, j whereas I, J indices stand for the nuclei of a system containing N electrons and L nuclei. Coordinates corresponding to the electrons are $\mathbf{r}_i$ for $i = 1, 2, 3, \dots, N$ whereas the coordinates of the nuclei are represented by $\mathbf{R}_I$ for $I = 1, 2, 3, \dots, L$.

By making use of the Hartree atomic units such that $m_e = \hbar = 4\pi\epsilon_0 = e = 1$, Eq. 2.3 reduces to the following one.

$$\begin{aligned} \hat{H} = & -\frac{1}{2} \sum_i^N \nabla_i^2 + \frac{1}{2} \sum_i^N \sum_{i \neq j}^N \frac{1}{|\mathbf{r}_i - \mathbf{r}_j|} - \sum_i^N \sum_I^L \frac{Z_I}{|\mathbf{r}_i - \mathbf{R}_I|} \\ & + \frac{1}{2} \sum_I^L \sum_{I \neq J}^L \frac{Z_I Z_J}{|\mathbf{R}_I - \mathbf{R}_J|} \end{aligned} \quad (2.4)$$

To write the Hamiltonian written in the equation above in a much more compact way, naming each term in Eq. 2.4 may be useful. In Eq. 2.4, the first term is the kinetic energy term corresponding to N electrons and denoted as $\hat{K}_e$, the second one is the potential that describes the interaction of electrons with each other and written as $\hat{V}_{ee}$, the third term represents the interaction between electrons and nuclei that is denoted by $\hat{V}_{eN}$, and the last term is nucleus-nucleus interaction term that is indicated as $\hat{V}_{NN}$. Therefore, the Hamiltonian can be written in a simpler form as obtained in Eq. 2.5.

$$\hat{H} = \hat{K}_e + \hat{V}_{ee} + \hat{V}_{eN} + \hat{V}_{NN} \quad (2.5)$$

So far, $\hat{H}$ is partly simplified using the Born-Oppenheimer approximation. However, more approximation is needed to solve the (time-independent) Schrödinger equation since it is still difficult to solve due to the degrees of freedom that has which is $3N$. Recall the Schrödinger equation in Eq. 2.2. Since there are N electrons in the system, the wave function that describes them contains coordinates corresponding to electrons which were $\mathbf{r}_i$ for $i = 1, 2, 3, \dots, N - 1, N$. Therefore, the many-electron wave function describing the system may be written as follows (without spin components).

$$\psi = \psi(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_{N-1}, \mathbf{r}_N) \quad (2.6)$$

For electrons, by using the Hartree atomic units, the electronic Schrödinger equation is written in terms of electronic Hamiltonian that is given in Eq. 2.7, and electronic wave function ψ_e .

$$\hat{H}_e = -\frac{1}{2} \sum_i^N \nabla_i^2 + \frac{1}{2} \sum_i^N \sum_{i \neq j}^N \frac{1}{|\mathbf{r}_i - \mathbf{r}_j|} - \sum_i^N \sum_I^L \frac{Z_I}{|\mathbf{r}_i - \mathbf{R}_I|} \quad (2.7)$$

2.2 Hohenberg-Kohn (HK) Theorems and the Kohn-Sahm Equation

By utilizing the electron density which depends on three spatial variables instead of dealing with many-electron wave functions that have $3N$ variables without the spin, the fundamentals of DFT are based on the two Hohenberg-Kohn Theorems: First HK Theorem and Second HK Theorem [59, 60, 61, 62]. Notice that $\hat{V}_{eN}$ in Eq. 2.5 may be called the external potential as well and denoted by $\hat{V}_{ext}$. The reason behind this terminology is explained now. By the Born-Oppenheimer approximation, the positions of the nuclei are assumed to be fixed which enables

electrons to regard that Coulomb interaction as an external potential.

$$\hat{V}_{ext} = \hat{V}_{eN} = - \sum_{i=1}^N \sum_{I=1}^L \frac{Z_I}{|\mathbf{r}_i - \mathbf{R}_I|} \quad (2.8)$$

First HK Theorem states that there is a unique one-to-one relation between the non-degenerate ground state electron density and the external potential $\hat{V}_{ext}$ which is the potential term displaying the interactions between the electrons and nuclei. This theorem is vital in DFT to construct the Hamiltonian of the system. When the Hamiltonian is described, by the Schrödinger equation, the wave function and the energy eigenvalues are found by solving this partial differential equation which is an eigenvalue-eigenvector equation [62].

The second HK Theorem stresses the variational principle. In the Hamiltonian provided in Eq. 2.5, terms corresponding to the kinetic energy of non-interacting electrons ($E_K[n]$) and interactions of electrons with each other ($E_{ee}[n]$) can be written in terms of the electron density at zero Kelvin which does not depend on the position of nuclei or the number of electrons present in the system [60]. The energy functional $E_v[n]$ which is a functional of the density, can be expressed in terms of a definite introduced static external potential that is $v(\mathbf{r})$.

$$E_v[n] = \int n(\mathbf{r})v(\mathbf{r}) d\mathbf{r} + F[n] \quad (2.9)$$

where $F[n]$ is the universal functional.

$$F[n] = E_K[n] + E_{ee}[n] \quad (2.10)$$

$$N = \int n(\mathbf{r}) d\mathbf{r} \quad (2.11)$$

where N is the total number of electrons. When the actual value of the electronic charge density has been determined, the energy functional becomes the ground state energy, E_0 which has the minimum energy.

$$n(\mathbf{r}) = N \int |\psi(\mathbf{r}, \mathbf{r}_2, \dots, \mathbf{r}_{N-1}, \mathbf{r}_N)|^2 d\mathbf{r}_2 d\mathbf{r}_3 \cdots d\mathbf{r}_{N-1}, d\mathbf{r}_N \quad (2.12)$$

Eq. 2.12 is stating the electron density $n(\mathbf{r})$. Notice that integration is not performed over the spatial variable corresponding to the first corpuscle in the system [62]. Integration has done over $\mathbf{r}_i$ where $i = 2, 3, \dots, N - 1, N$. Electron density and electronic charge density are interconnected. For a charge q , electronic charge density is written as below.

$$\rho(\mathbf{r}) = qn(\mathbf{r}) \quad (2.13)$$

The demanding part is obtaining $F[n]$ [60]. Hohenberg and Kohn defined this universal functional as below.

$$F[n] = \frac{1}{2} \int \frac{n(\mathbf{r})n(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r}d\mathbf{r}' + G[n] \quad (2.14)$$

where $G[n]$ is another universal functional [60]. Substitution of $F[n]$ into the energy functional equation, the equation below is obtained.

$$E_v[n] = \int d\mathbf{r} v(\mathbf{r})n(\mathbf{r}) + \frac{1}{2} \int \frac{n(\mathbf{r})n(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r}d\mathbf{r}' + G[n] \quad (2.15)$$

In the ground state, $E_v[n]$ becomes E_0 and has the minimum value so that for the true value of the density, energy indicated in Eq. 2.15 is minimized. In the publication of Kohn and Sham, they suggested an approximation for $G[n]$ that is expressed as in Eq. 2.16 by including the exchange-correlation (XC) energy which is a functional of the electron density [61].

$$G[n] = E_K[n] + E_{xc}[n] \quad (2.16)$$

where XC functional is exhibited in Eq 2.17.

$$E_{xc}[n] = \int d\mathbf{r} n(\mathbf{r}) \epsilon_{xc}(n(\mathbf{r})) \quad (2.17)$$

$\epsilon_{xc}(n(\mathbf{r}))$ in Eq. 2.17 represents the XC energy/electron [61]. The variational principle corresponding to the second HK theorem applies:

$$E_0 \leq E_v[\rho] \quad (2.18)$$

where the ground state energy E_0 corresponds to $E_v[\rho = \rho_0]$ since ρ_0 is the electronic charge density at the ground state. To approximate the Schrödinger equation, functionals in Eq. 2.16 should be determined to construct the Hamiltonian. However, to do that, Kohn and Sham came up with the idea of writing many-body wave functions in terms of single-particle wave functions which work accurately in DFT calculations [61]. Let us denote the Kohn-Sham orbitals (wave functions) as $\phi_i(\mathbf{r})$, then, the density that is acquired by the expectation value of the operator $\hat{\rho}$, and the Kohn-Sham equation which contains Kohn-Sham Hamiltonian ($\hat{H}_{KS}$) are written as in the following form.

$$\rho(\mathbf{r}) = \langle \phi_i(\mathbf{r}) | \hat{\rho}(\mathbf{r}) | \phi_i(\mathbf{r}) \rangle \quad (2.19)$$

$$\hat{H}_{KS}\phi_i(\mathbf{r}) = E_{KS}\phi_i(\mathbf{r}) \quad (2.20)$$

Electron density is expressed as:

$$n(\mathbf{r}) = \sum_{i=1} |\phi_i(\mathbf{r})|^2 \quad (2.21)$$

Single-particle wave functions should be represented using a finite basis set to solve the Kohn-Sham equation. Throughout this thesis, Quantum ESPRESSO software is utilized which uses the plane wave expansion [65, 66, 67].

For simplification, energy functional can be written by using two terms: the XC functional denoted by $\tilde{E}_{XC}$, and energy terms that do not include XC denoted by $\tilde{E}$. $\tilde{E}_{XC}$ term of the energy functional contains the contributions belonging to quantum mechanics which is not contained in $\tilde{E}$. However, $\tilde{E}$ contains electron-electron interaction, kinetic energy corresponds to the electrons, nuclei-nuclei interaction, and electron-nucleus interaction terms. Therefore, the Kohn-Sham Hamiltonian includes $\hat{V}_{eN}$, XC potential $\hat{V}_{XC}$ that is the functional derivative of the exchange-correlation energy, and Hartree potential $\hat{V}_H$ terms [68].

$$V_H(\mathbf{r}) = \int \frac{n(\mathbf{r}')d\mathbf{r}'}{|\mathbf{r} - \mathbf{r}'|} \quad (2.22)$$

DFT uses the following algorithm to solve the Kohn-Sham equation in a self-consistent iterative way.

1. A starting electron density is defined.
2. By solving the Kohn-Sham equation using the starting electron density, the single-electron wave functions are obtained.
3. Once single-electron wave functions are determined, new electron density $n_{new}(\mathbf{r})$ is obtained by using Eq. 2.21.
4. As a final step, $n(\mathbf{r})$ and $n_{new}(\mathbf{r})$ are compared. When those two densities are not equal, the same iterative procedure continues by updating the electron density until they become equal to each other. When the densities become equal to each other, the total energy is calculated by DFT and other desired properties can be obtained [68].

2.3 XC Functionals

To be able to solve the Kohn-Sham equation, XC functional should be determined since the Hamiltonian includes that term. XC functionals are not-known functionals that are approximated in various kinds according to the need in the system. They arise due to the antisymmetry in the wave functions. I briefly mention widely used a few of them. Local density approximation (LDA) utilizes sole local electron density for approximating XC functional and can be expressed mathematically by using Eq. 2.17 and obtained in Eq. 2.23 [68].

$$E_{xc}^{\text{LDA}} = \int d\mathbf{r} n(\mathbf{r}) \epsilon_{xc}(n(\mathbf{r})) \quad (2.23)$$

Another widely used XC functional is generalized gradient approximation (GGA). GGA utilizes the local contribution coming from LDA and additionally includes the gradient of the density of electrons [68, 69]. GGA can be expressed mathematically as:

$$E_{xc}^{\text{GGA}} = \int d\mathbf{r} n(\mathbf{r}) \epsilon_{xc}(n(\mathbf{r}), \nabla n(\mathbf{r})) \quad (2.24)$$

In all calculations performed in this thesis, including van der Waals interactions to calculations, VDW-DF2 is utilized as XC functional which includes non-local terms [70].

2.4 Pseudopotentials

In real space, to describe the rapidly oscillating plane waves, large amounts of energy cutoffs are required which makes the computation more expensive. Mostly, core electrons are responsible for those mentioned rapid oscillations. However, material properties are mainly described by the valance electrons [68]. Therefore, this may be a good idea to not include the inner shell electron contributions separately, and merge their effects using an effective potential, i.e., a pseudo-potential [71]. This problem is solved by using pseudo-potentials. There are different kinds of pseudo-potentials in the literature and they can have different application areas. Some of them deduce the band gap of materials is larger than it is, and some of them underestimate it. By testing different pseudo-potentials, XC functionals, or by investigating what scientist did in their works, the more optimal parameters can be determined. Details about the utilized pseudopotentials are provided at the beginning of the chapters.

Chapter 3

Electronic and Optical Properties of Monolayer Graphene under the Perpendicular Static Electric Field

In this chapter, the effects of the external static electric field (E-field) on monolayer graphene are investigated. E-field is applied along the z-axis, that is the axis perpendicular to the graphene layer with various amplitudes changing from 0.1 V/Å to 2.5 V/Å. Geometry optimizations, electronic properties including electronic band structure and local density of states (DOS) calculations, and optical properties together with the imaginary part of the dielectric function ($Im(\varepsilon(\omega))$, namely ε_2), and real part of dielectric function (ε_1) are investigated by the ground state calculations from first principles based on DFT. Notice that the DOS term corresponds to the local density of states. All of the calculations have been performed using Quantum ESPRESSO (QE) software [65, 66, 67]. Ground state self-consistent field calculations have been performed using pw.x code to solve Kohn-Sham equations iteratively. For investigating the interconnection between light (electromagnetic wave) with material, the imaginary part of the dielectric

function is used. To determine necessary matrix elements corresponding to optical quantities, epsilon.x code [72] is implemented to obtain interband transitions between electronic states (from occupied to unoccupied ones) in the presence of the external electric field both in-plane and out-of-plane directions. Electronic and optical results obtained under the E-field are compared with those in the absence of the E-field. In the following interpretation, I use the E-field term for the case when there is an external static electric field is present, and the no-E-field term for the case when the external electric field is absent.

3.1 Electronic Properties

After performing several convergence tests for Monkhorst-Pack k-mesh sampling [73] and kinetic energy cutoff for the plane-waves following parameters are chosen throughout the indicated calculations involving SCF, structural optimization, and DOS. In all calculations, the convergence threshold for the total energy is used as 1×10^{-8} Ry. The distance between nearest-neighboring carbon atoms is determined as 1.428 Å after geometry optimization. For the structural optimization, the convergence threshold for the forces is used as 1×10^{-3} Ry, whereas the convergence threshold for stress was 0.5 kbar. To prevent possible interactions between graphene layers a vacuum of 24 Å has been introduced to the unit cell along the z-axis. Carbon atoms are described by norm-conserving pseudo-potential [74]. For investigation of van der Waals interactions, VDW-DF2 [70] is used as the exchange-correlation functional. For structural optimization and electronic band structure calculations, the first Brillouin zone is sampled on a 29x29x1 Monkhorst-Pack k-mesh, whereas for DOS calculations k-mesh sampling was 48x48x1. The kinetic energy cutoff for the plane waves was determined as 90 Ry. For metallic systems, smearing is desired. To smoothen the electronic state occupations near the Fermi level, Gaussian smearing is used while performing SCF and optical calculations whereas for obtaining electronic states corresponding to DOS, the tetrahedron technique is utilized.

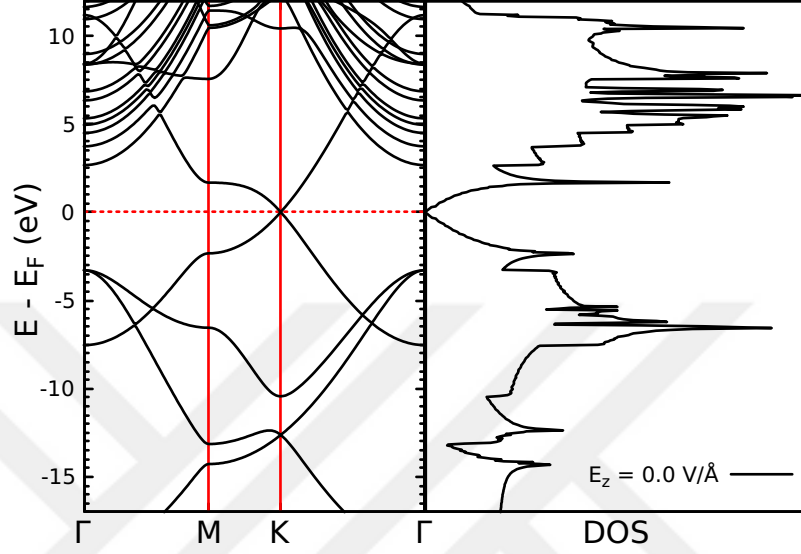


Figure 3.1: Electronic band diagram and DOS of monolayer graphene in the absence of external fields.

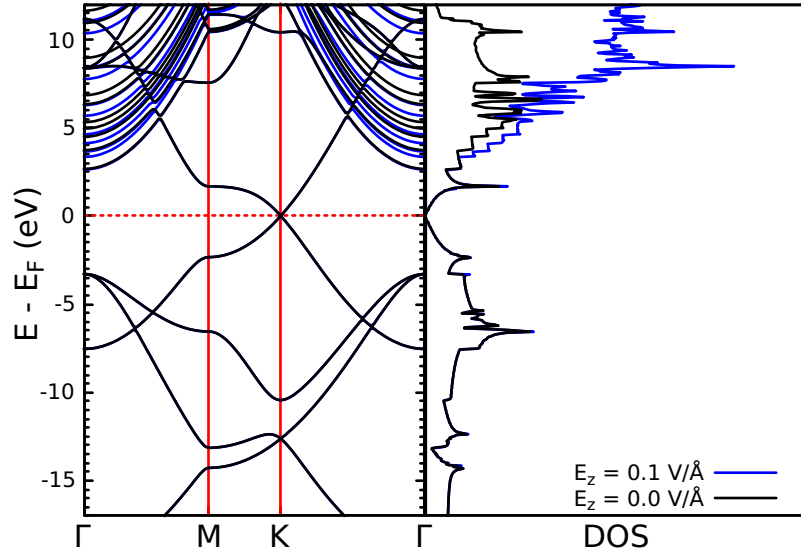


Figure 3.2: Electronic band structure and DOS of monolayer graphene under an external electric field of magnitude $E_z=0.1 \text{ V/\AA}$.

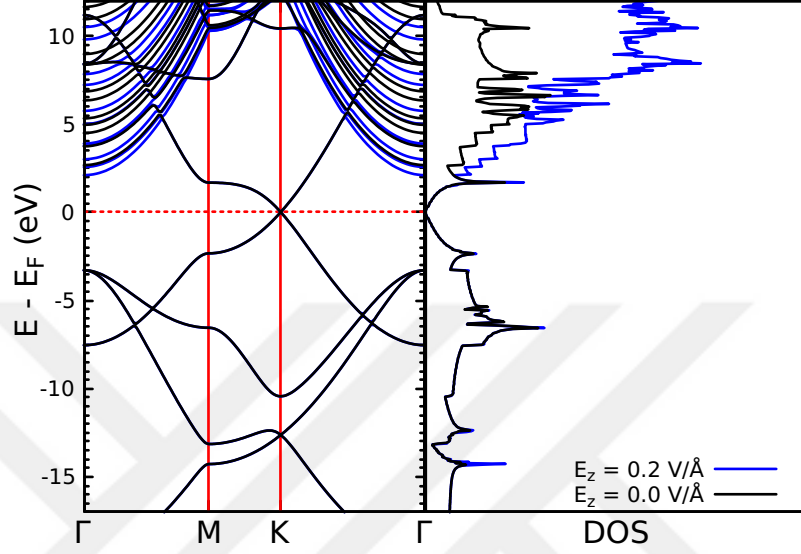


Figure 3.3: Electronic band diagram and DOS of monolayer graphene in the presence of E-field of strength $E_z=0.2 \text{ V/Å}$.

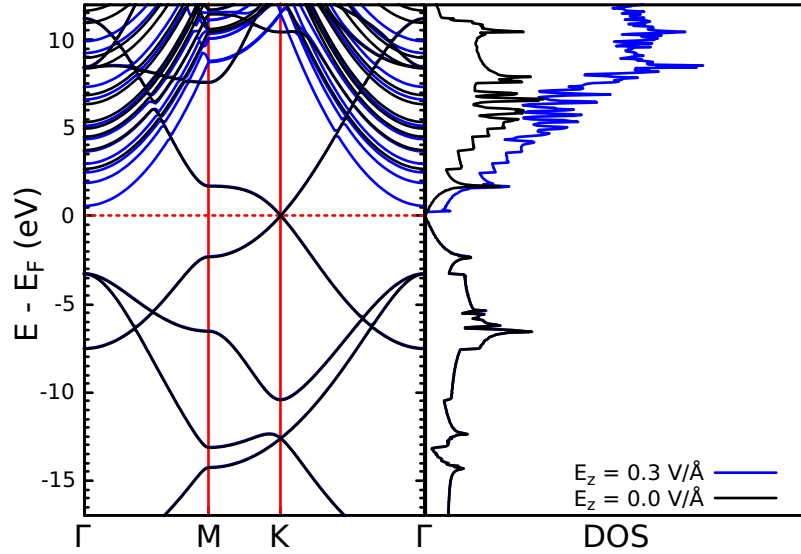


Figure 3.4: Electronic band structure and DOS of monolayer graphene under an E-field strength of $E_z=0.3 \text{ V/Å}$.

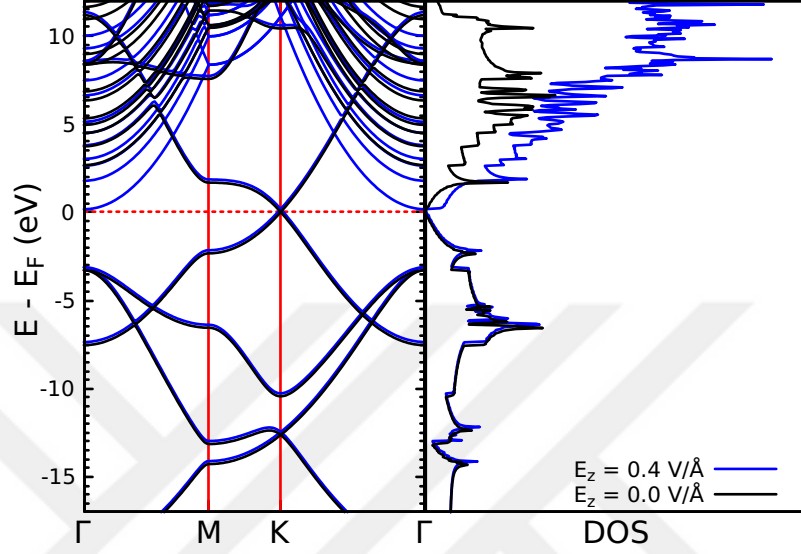


Figure 3.5: Electronic band diagram and DOS of monolayer graphene under $E_z=0.4 \text{ V/\AA}$.

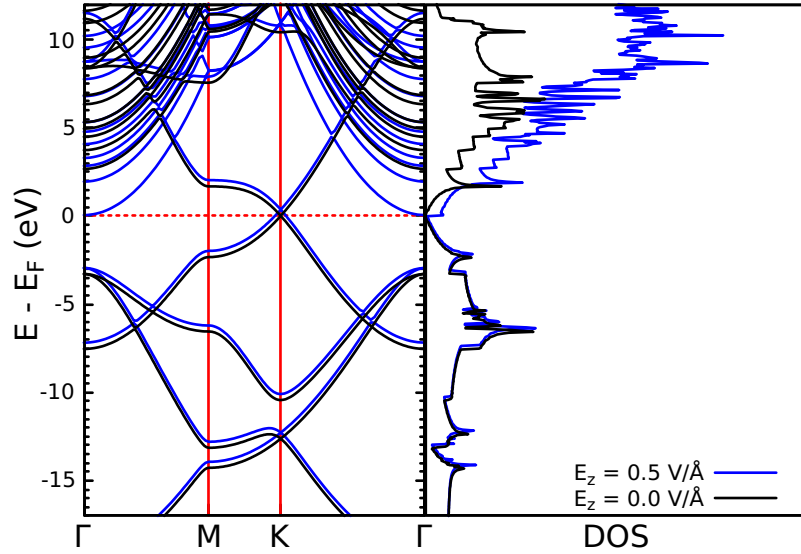


Figure 3.6: Electronic band diagram and DOS of monolayer graphene in the presence of an external electric field of magnitude $E_z=0.5 \text{ V/\AA}$.

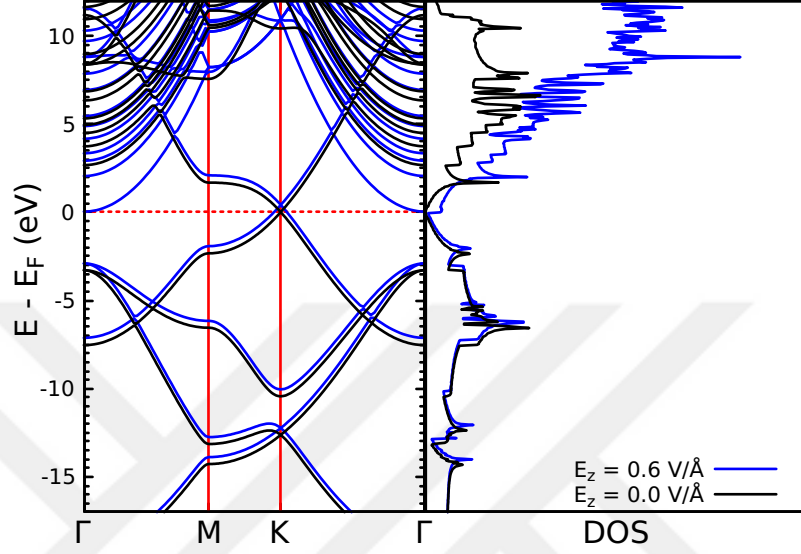


Figure 3.7: Electronic band diagram and DOS of monolayer graphene under $E_z=0.6 \text{ V/\AA}$.

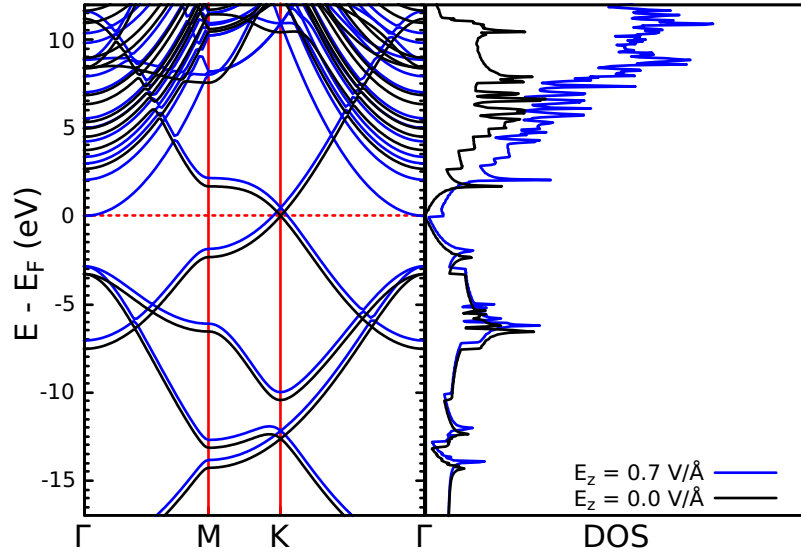


Figure 3.8: Electronic band diagram and DOS of monolayer graphene under the influence of an E-field of $E_z=0.7 \text{ V/\AA}$.

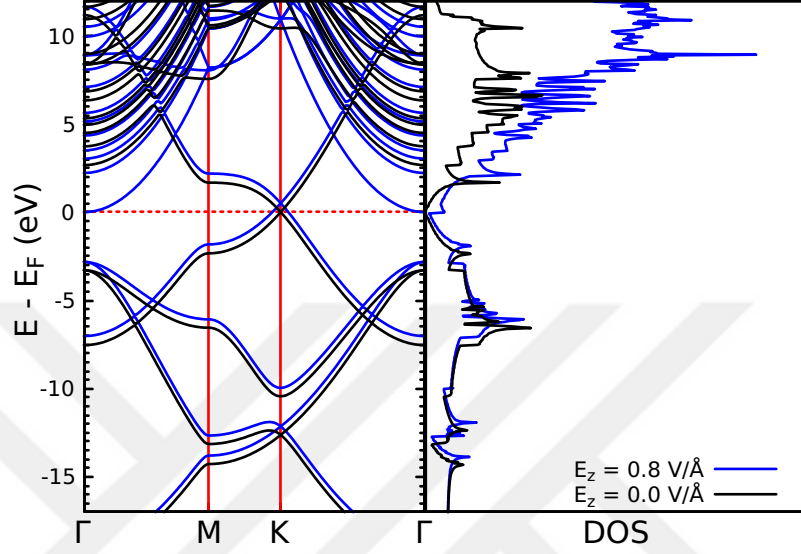


Figure 3.9: Electronic band diagram and DOS of monolayer graphene under the E-field of magnitude $E_z=0.8 \text{ V/\AA}$.

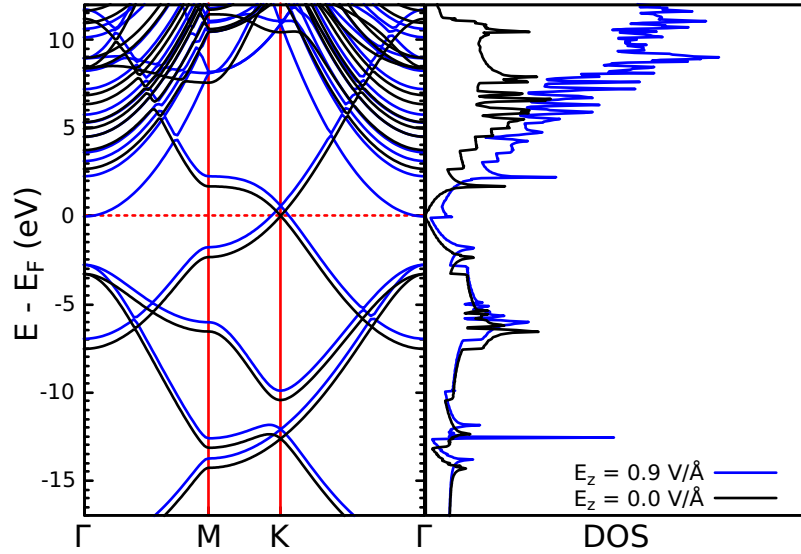


Figure 3.10: Electronic band diagram and DOS of monolayer graphene under $E_z=0.9 \text{ V/\AA}$.

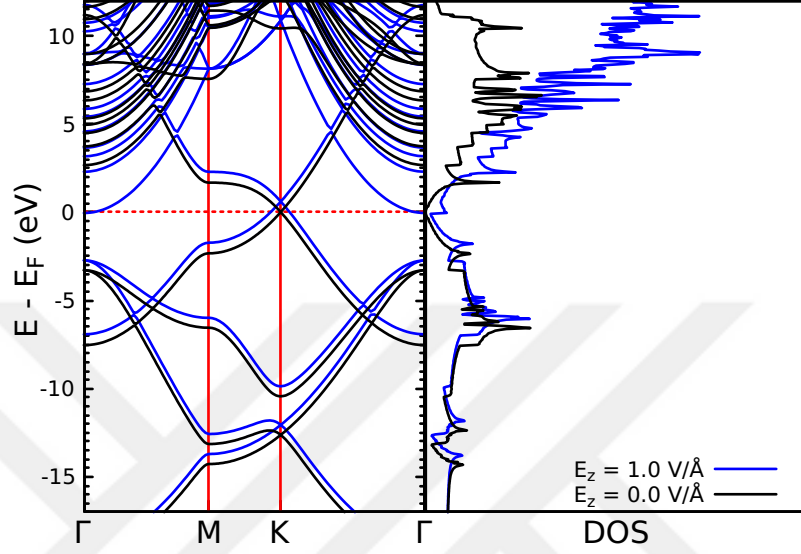


Figure 3.11: Electronic band diagram and DOS of monolayer graphene in the presence of an external electric field of magnitude $E_z=1.0 \text{ V/\AA}$.

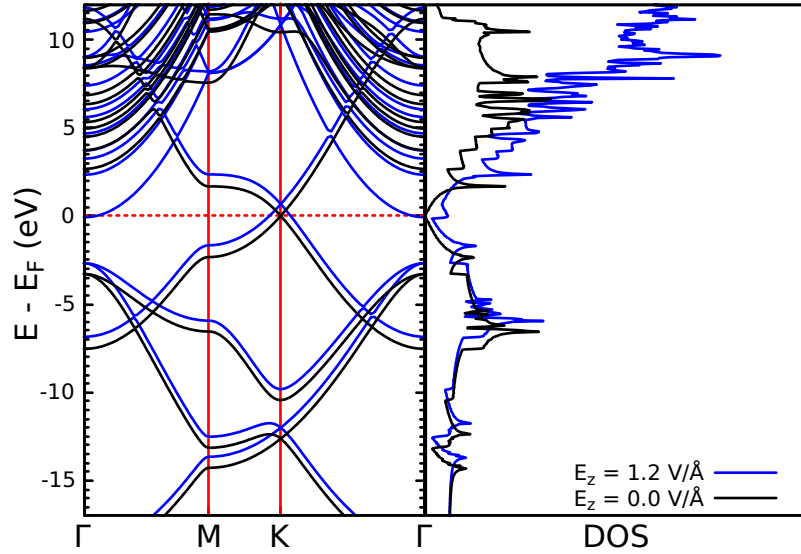


Figure 3.12: Electronic band diagram and DOS of monolayer graphene under $E_z=1.2 \text{ V/\AA}$.

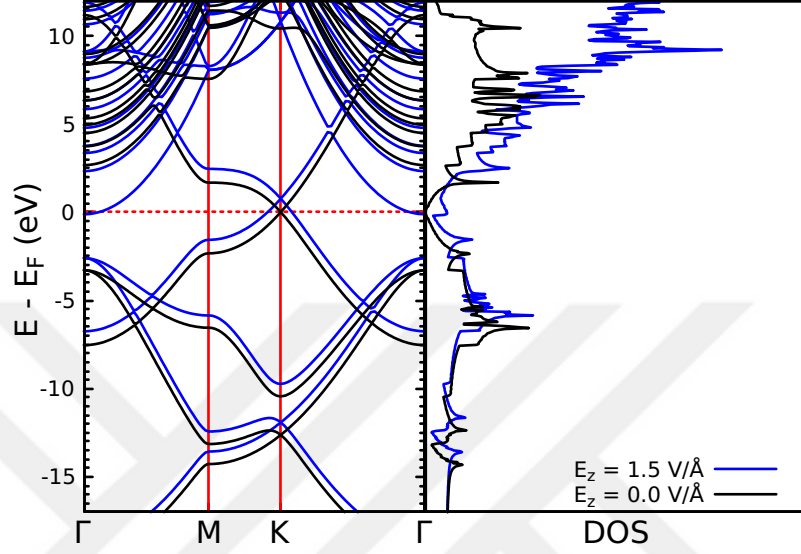


Figure 3.13: Electronic band diagram and DOS of monolayer graphene under the E-field of magnitude $E_z=1.5 \text{ V/\AA}$.

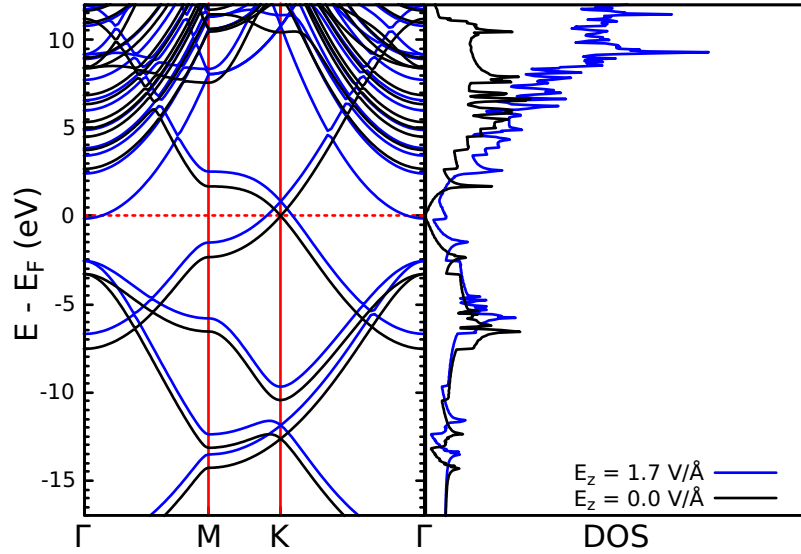


Figure 3.14: Electronic band structure and DOS of monolayer graphene under the perpendicular electric field of magnitude $E_z=1.7 \text{ V/\AA}$.

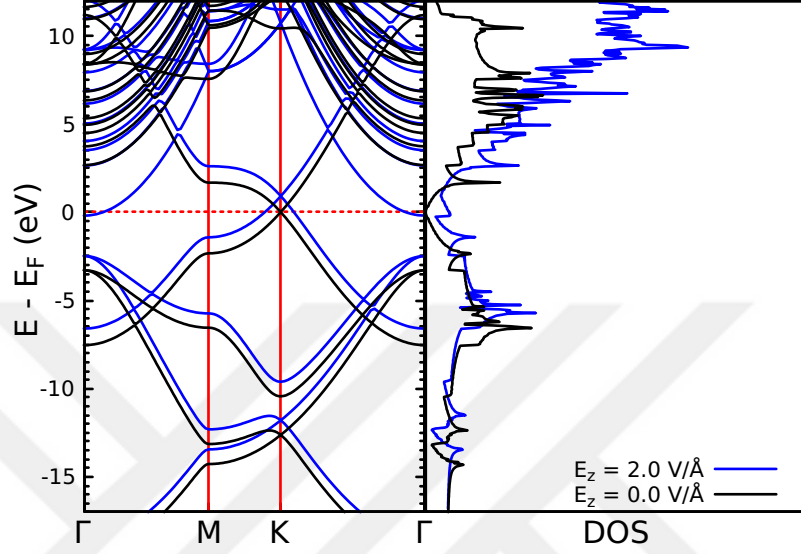


Figure 3.15: Electronic band diagram and DOS of monolayer graphene under the influence of an E-field of $E_z=2.0 \text{ V/\AA}$.

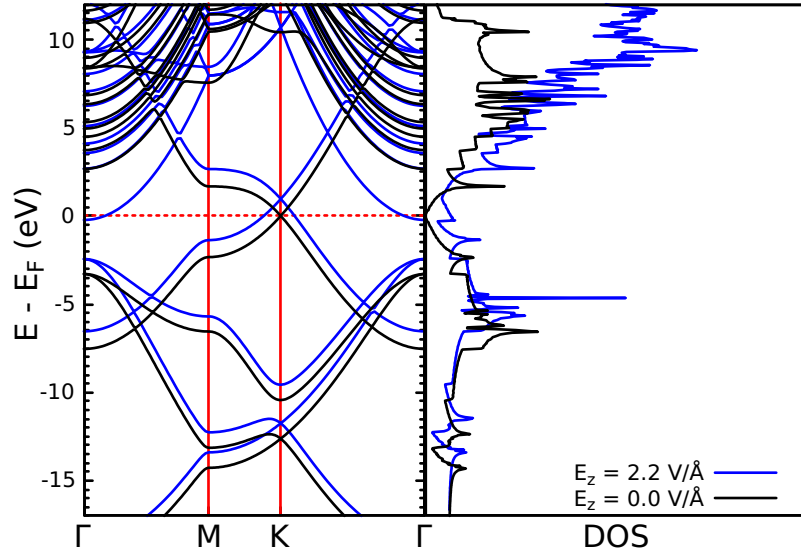


Figure 3.16: Electronic band diagram and DOS of monolayer graphene under the E-field of magnitude $E_z=2.2 \text{ V/\AA}$.

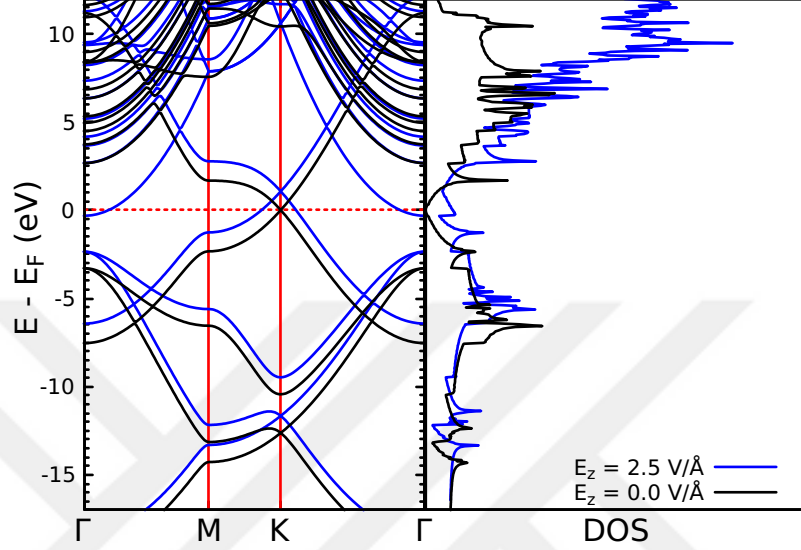
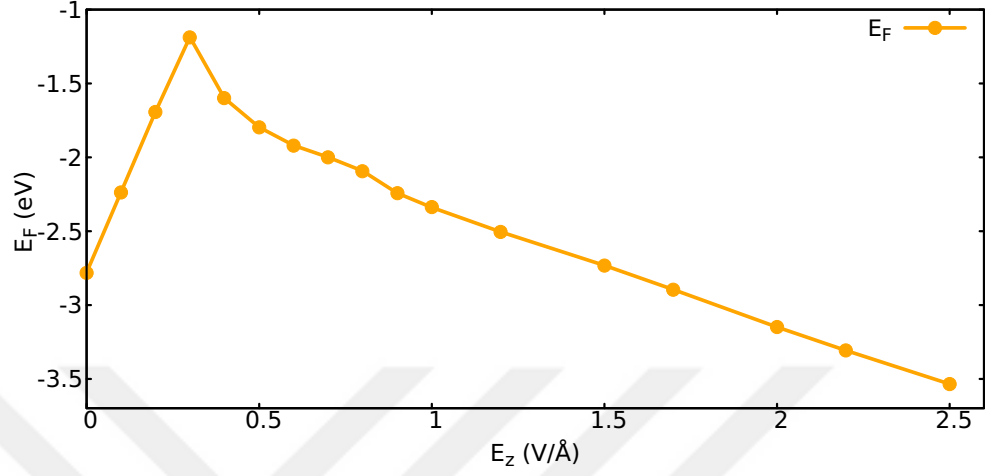


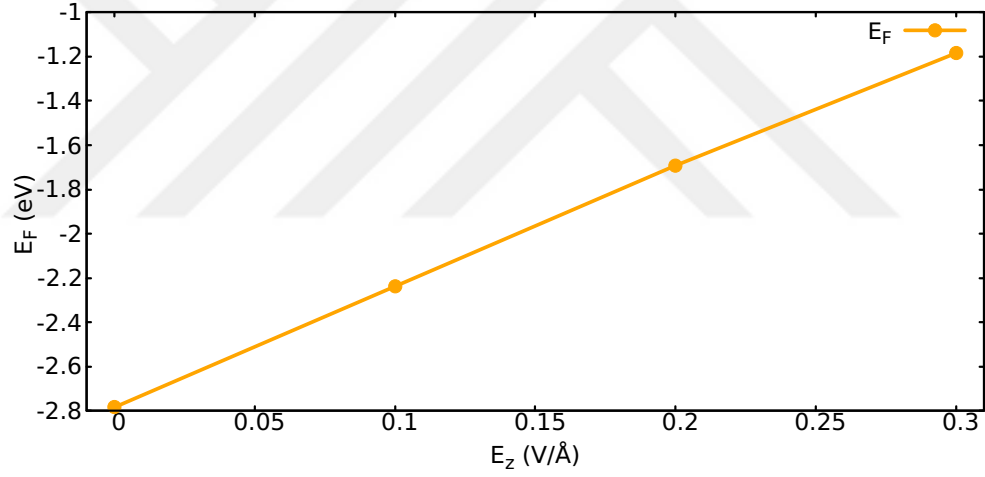
Figure 3.17: Electronic band diagram and DOS of monolayer graphene under the influence of $E_z=2.5$ V/Å.

As mentioned in Chapter 1, when an external electric field (or an external bias) is applied to the system, Fermi energy E_F becomes shifted and the electrons are transferred from occupied states to the unoccupied ones. From the self-consistent field (SCF) calculations shifts in Fermi energy with varying amplitudes of the applied E-field are obtained as indicated in Fig. 3.18a. For $0.0 \text{ V/Å} \leq E_z \leq 0.3 \text{ V/Å}$, E_F increased linearly (Fig. 3.18b). However, for $0.9 \text{ V/Å} \leq E_z \leq 2.5 \text{ V/Å}$, there is an almost linear decrease in E_F . After $E_z \geq 0.4 \text{ V/Å}$, E_F continued decreasing up to 2.5 V/Å . Additionally, for $0.4 \text{ V/Å} \leq E_z \leq 0.8 \text{ V/Å}$, E_F decreased but in a non-linear fashion.

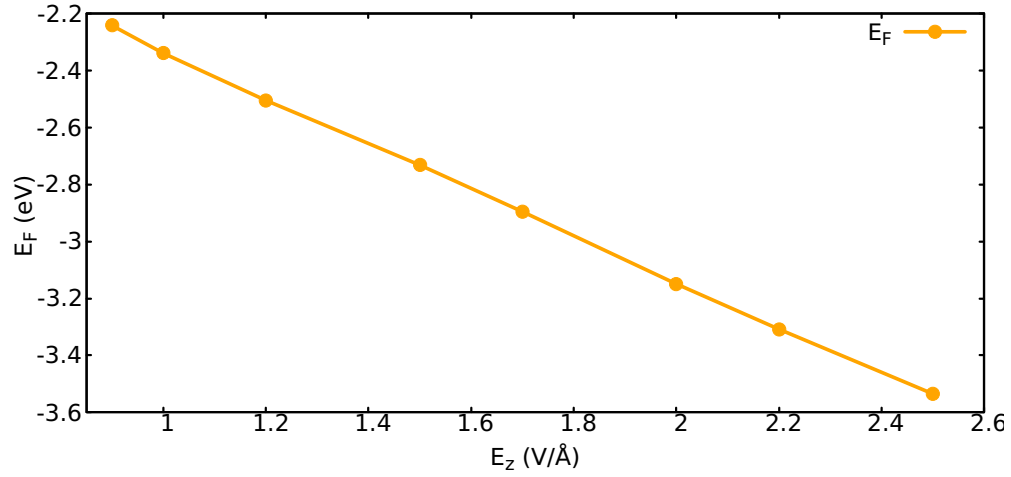
In Table 3.1 energy difference between E_F at K point in the first Brillouin zone (fBZ) in the absence ($E_F^{no-field}$) and presence (E_F^{field}) of E-field is tabulated and denoted by ΔE such that $\Delta E = E_F^{field} - E_F^{no-field}$. Fermi level shifted upwards for all E-field magnitudes except for $E_z = 0.2 \text{ V/Å}$. For $E_z = 0.2 \text{ V/Å}$, E_F shifted 0.00286 eV downwards and that shift is indicated with a minus sign in Table 3.1. Except for $E_z = 0.2 \text{ V/Å}$, shift in E_F and ΔE increased by increasing E-field.



(a)



(b)



(c)

Figure 3.18: Change in Fermi energy due to distinct values of amplitudes corresponding to the applied electric field. (a) $0.0 \text{ V/Å} \leq E_z \leq 2.5 \text{ V/Å}$. (b) $0.0 \text{ V/Å} \leq E_z \leq 0.3 \text{ V/Å}$. (c) $0.9 \text{ V/Å} \leq E_z \leq 2.5 \text{ V/Å}$.

E_z (V/Å)	ΔE (eV)
0.1	0.00288
0.2	-0.00286
0.3	0.0386
0.4	0.175
0.5	0.353
0.6	0.405
0.7	0.465
0.8	0.503
0.9	0.560
1.0	0.601
1.2	0.667
1.5	0.760
1.7	0.821
2.0	0.904
2.2	0.958
2.5	1.06

Table 3.1: ΔE values obtained from electronic band structure calculations for all applied E-field amplitudes.

In electronic band structure and DOS plots, Fermi energy is set to zero. VB in Fig. 3.2, Fig. 3.3 and Fig. 3.4 are almost degenerate whether an external E-field is present or not, whereas shifts in the CB started to occur in these figures which were for $E_z=0.1$ V/Å, $E_z=0.2$ V/Å and $E_z=0.3$ V/Å, respectively. Moreover, no significant changes were observed in the DOS in Fig. 3.2 and Fig. 3.3. Starting from Fig. 3.5 corresponding to $E_z=0.4$ V/Å, degeneracy in VB is broken and the bands corresponding to p_z orbitals, namely, π and π^* bonds shifted upwards due to the external E-field. The decline in E_F after $E_z=0.3$ V/Å relates to the broken degeneracy for the values above $E_z=0.3$ V/Å in the electronic band diagrams. Moreover, after $E_z=0.3$ V/Å (Fig. 3.4), van Hove singularities are observed which appear as new structures in DOS in addition to those that were already present without any field effects in Fig. 3.1. Van Hove singularities occur in the electronic structure of the materials due to the saddle points existing in the electronic band structure. Apparently, by applying an external electric field to a

material, one may change its optical and electronic features [8]. Hence, van Hove singularities observed in the DOS of monolayer graphene allow electrons to fill more electronic states. For $E_z=0.5$ V/Å and greater E-field amplitudes, starting from Fig. 3.6, band corresponding to antibonding sp^2 orbital, namely, σ^* band, reached below the Fermi level since the bands with blue color (shifted bands due to external E-field) are touching to the red dotted curve which is indicating the Fermi level. This circumstance is apparent by the DOS plots as well since it is shifted to -0.015 eV. Starting from $E_z=0.5$ V/Å, that is Fig. 3.6, the Fermi level is populated and the amount of population increased as the strength of the external E-field increased and σ^* band started to move below E_F . Therefore, for $E_z \geq 0.5$ V/Å, due to the significant shift of σ^* band, more available electronic states are revealed for electrons to fill in which enables us to dope monolayer graphene accordingly that is discussed in Chapter 3.2. This circumstance continued by increasing E-field amplitudes up to Fig. 3.17.

3.2 Optical Properties

The imaginary part of the dielectric function is utilized to investigate the interconnection between light with material. Optical quantities are calculated by implementing epsilon.x code in QE in order to obtain interband transitions in the presence of the E-field. Reducing the k-points grid to the irreducible Brillouin zone is a lack of epsilon.x code, therefore, k-points are used with equal weights with a steady grid by writing coordinates and equal weights manually using the crystal option [72]. SCF calculations are also repeated using the crystal option. The number of manually written coordinates is taken as 576 since the number of k-points along x- and y- directions are chosen as 24, and it is chosen as 1 for the z-direction which makes 576 coordinates in total.

While electromagnetic waves are propagating within the materials, they oscillate so that they make electric dipoles oscillate as well. Mentioned dipoles might be either between the atoms or inside the atom. Those dipoles may be

coupled with the external field and the field due to other dipoles [75]. Induced polarization $\mathbf{P}$ is directly related to the electric field $\mathbf{E}$ and given in Eq. 3.1.

$$\mathbf{P} = \varepsilon_0 \chi_e \mathbf{E} \quad (3.1)$$

χ_e in Eq. 3.1 is a dimensionless constant called electric susceptibility and is related to the relative electric permittivity ($\frac{\varepsilon}{\varepsilon_0}$) as written in Eq. 3.2 [76].

$$\frac{\varepsilon}{\varepsilon_0} = 1 + \chi_e \quad (3.2)$$

where ε_0 is the permittivity corresponding to free space. The displacement field $\mathbf{D}$, that is the total macroscopic field, is described in Eq. 3.3.

$$\mathbf{D} = \varepsilon_0 \mathbf{E} + \mathbf{P} \quad (3.3)$$

Using Equations 3.1, 3.2, 3.3 displacement field and electric field relation is given as below.

$$\mathbf{D} = \varepsilon \mathbf{E} \quad (3.4)$$

Fermi's golden rule (FGL) is used to determine interband transitions. Dielectric function $\varepsilon(\omega)$, and FGL formulas are given in Equations 3.5 and 3.6, respectively. Dielectric function is a physical quantity that consists of real and imaginary parts and contains information about the behavior of a system under an external electric field. Therefore, to investigate interband transition both in the absence and presence of the E-field, it is a logical choice to perform optical calculations regarding dielectric function data.

$$\epsilon(\omega) = \epsilon_1(\omega) + i\epsilon_2(\omega) \quad (3.5)$$

$$\epsilon_2(\omega) \propto \sum_{v,c,\mathbf{Q}} (\langle c, \mathbf{Q} | \mathbf{v} \cdot \mathbf{r} | v, \mathbf{Q} \rangle) (\langle v, \mathbf{Q} | \mathbf{r} \cdot \mathbf{v} | c, \mathbf{Q} \rangle) \delta(E_{c,\mathbf{Q}} - E_{v,\mathbf{Q}} - \hbar\omega) \quad (3.6)$$

where $\mathbf{Q}$ is the momentum given to the system, $\mathbf{r}$ is the position operator, $\mathbf{v}$ is the velocity operator, v represents states in the valance band, c stands for the states in the conduction band, $|v, \mathbf{Q}\rangle$ describes electronic states in the valance band, and $|c, \mathbf{Q}\rangle$ describes electronic states in the conduction band. Equation 3.6 is

nonzero when the delta function is nonzero implying that the difference between $E_{c,\mathbf{Q}}$ and $E_{v,\mathbf{Q}}$ equals to the energy of photon that is $\hbar\omega$.

ε_2 is interconnected with electron energy loss (EEL) cross-section and absorption of light [77]. Therefore, EEL spectroscopy is one of the methods, as well as absorption, to obtain optical properties associated with the dielectric function. Using the perturbation theory, the complex part of dielectric tensor $\varepsilon_{2,\alpha\beta}(\omega)$ can be obtained as follows.

$$\varepsilon_{2,\alpha\beta}(\omega) = \frac{4\pi e^2}{\Omega N_{\mathbf{k}} m^2} \sum_{v,c} \sum_{\mathbf{k}} |\langle u_{\mathbf{k},v} | \hat{\mathbf{p}} | u_{\mathbf{k},c} \rangle|^2 \frac{f(E_{\mathbf{k},v}) - f(E_{\mathbf{k},c})}{(E_{\mathbf{k},c} - E_{\mathbf{k},v})^2} \delta(E_{\mathbf{k},c} - E_{\mathbf{k},v} - \hbar\omega) \quad (3.7)$$

In the presence of the electric field, due to the interconnection between material and the field, all excited electronic states will have a broadening which makes the statement in Eq. 3.7 not physical due to the fact that the measure of broadening Γ is required to be a finite and positive quantity. Γ provides information about the decaying time from excited states to the ground state, which is inversely proportional to the lifetime of a corresponding excited state τ . By assuming Γ is small, $\varepsilon_{2,\alpha\beta}(\omega)$ tensor is described by Drude-Lorentz dielectric tensor which is indicated in Eq 3.8. In the code that is implemented, Γ stands for intersmear broadening which corresponds to the data coming from interband transitions whereas η is intrasmear broadening due to intraband transitions. I only consider intersmear broadening and applied Gauissian kind of smearing. In the following equations, the frequency of the electromagnetic radiation is ω , $N_{\mathbf{k}}$ is the number of points corresponding to the frequency as implemented in the code, Ω is the volume of the defined cell, e is the electron charge, m is mass of the electron, $E_{\mathbf{k},v}$ represent energy eigenvalues corresponding to the Hamiltonian, $f(E_{\mathbf{k},v})$ is the function representing Fermi distribution, $\mathbf{k}$ is the momentum of electron, and $\hat{\mathbf{p}}$ is the momentum operator [72].

$$\begin{aligned}
\varepsilon_{2,\alpha\beta}(\omega) = & \frac{4\pi e^2}{m^2 \Omega N_{\mathbf{k}}} \sum_{v,\mathbf{k}} \left(\frac{df(E_{\mathbf{k},v})}{dE_{\mathbf{k},v}} \frac{\omega \eta \hat{\mathbf{M}}_{\alpha\beta}}{\omega^4 + \omega^2 \eta^2} + \dots \right) \\
& + \frac{8\pi e^2}{m^2 \Omega N_{\mathbf{k}}} \sum_{v \neq c} \sum_{\mathbf{k}} \frac{\hat{\mathbf{M}}_{\alpha\beta}}{E_{\mathbf{k},c} - E_{\mathbf{k},v}} \dots \\
& \times \frac{\omega \Gamma f(E_{\mathbf{k},v}) [(\omega_{\mathbf{k},c} - \omega_{\mathbf{k},v})^2 - \omega^2]}{[(\omega_{\mathbf{k},c} - \omega_{\mathbf{k},v})^2 - \omega^2]^2 + \omega^2 \Gamma^2}
\end{aligned} \tag{3.8}$$

$\hat{\mathbf{M}}_{\alpha,\beta}$ stands for the squared matrix elements of $\varepsilon_{\alpha\beta}(\omega)$ and given in Eq. 3.9.

$$\hat{\mathbf{M}}_{\alpha,\beta} = \langle u_{\mathbf{k},c} | \hat{\mathbf{p}}_{\alpha} | u_{\mathbf{k},v} \rangle \langle u_{\mathbf{k},v} | \hat{\mathbf{p}}_{\beta}^{\dagger} | u_{\mathbf{k},c} \rangle \tag{3.9}$$

In the optical calculations, firstly complex part of the dielectric function is calculated. Once ε_2 is obtained, ε_1 is determined by using the Kramers-Kronig relation [75, 76].

In this section, data related to the real and imaginary parts of dielectric function ($\varepsilon_1(\omega)$ and $\varepsilon_2(\omega)$, respectively) in the absence and presence of E-field are plotted. Both planar and vertical directions of polarization of light have been studied and indicated in the optical quantities cited above. For the real part of the dielectric function, $\varepsilon_1^{\perp}$ refers to the perpendicular direction of polarization (along the z-axis) whereas $\varepsilon_1^{\parallel}$ represents the polarization in the planar direction. Similarly, for the imaginary part of the dielectric function, $\varepsilon_2^{\perp}$ refers to the perpendicular direction of polarization whereas $\varepsilon_2^{\parallel}$ represents the polarization in the planar direction, i.e., along the graphene sheet. As mentioned in Chapter 1.1, π bonds correspond to the p_z orbitals whereas sp^2 orbitals are corresponding to $2s$, $2p_x$ and $2p_y$ orbitals [41]. Each C atom contributes one electron due to the p_z orbital which allows graphene to exhibit extraordinary properties [48]. After the implementation of epsilon.x, output files contain data related to the energy and diagonal matrix elements of ε_1 and ε_2 which are ε_{1xx} , ε_{1yy} , ε_{1zz} , ε_{2xx} , ε_{2yy} , and ε_{2zz} . For vertical polarization components ε_{1zz} and ε_{2zz} are used directly (Equations 3.12 and 3.13) whereas parallel components of ε_1 and ε_2 are calculated using Equations 3.10 and 3.11.

$$\varepsilon_1^{\parallel} = \frac{\varepsilon_{1xx} + \varepsilon_{1yy}}{2} \quad (3.10)$$

$$\varepsilon_2^{\parallel} = \frac{\varepsilon_{2xx} + \varepsilon_{2yy}}{2} \quad (3.11)$$

$$\varepsilon_1^{\perp} = \varepsilon_{1zz} \quad (3.12)$$

$$\varepsilon_2^{\perp} = \varepsilon_{2zz} \quad (3.13)$$

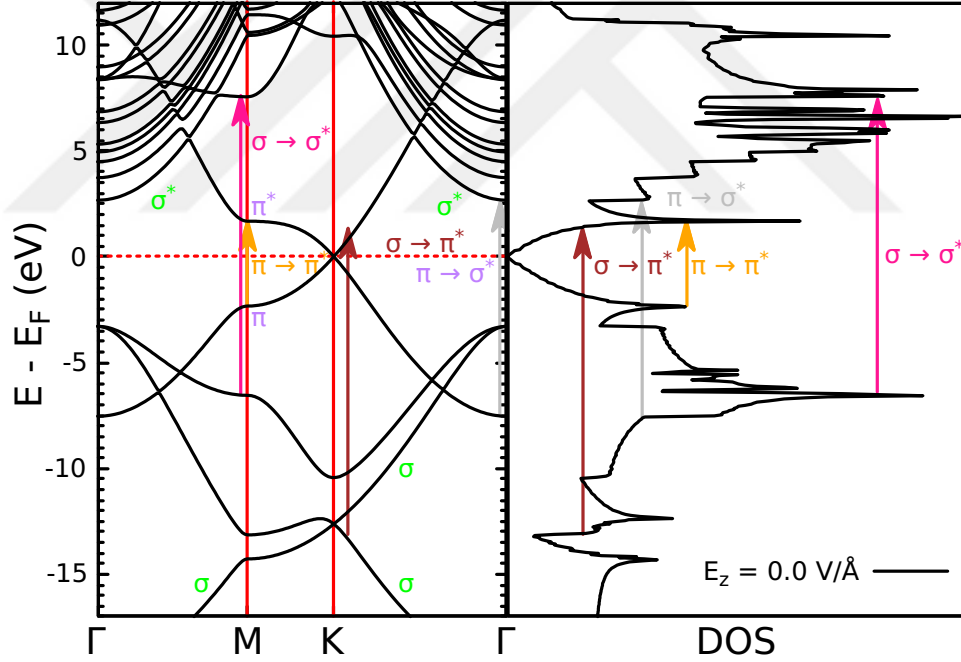
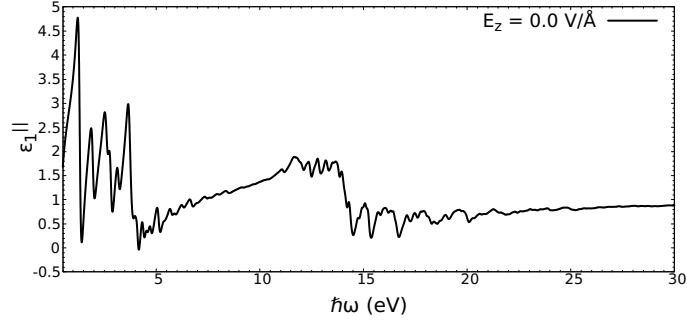


Figure 3.19: Electronic band structure and DOS of single-layer graphene in the absence of E-field that includes the interband transitions between VB and CB.

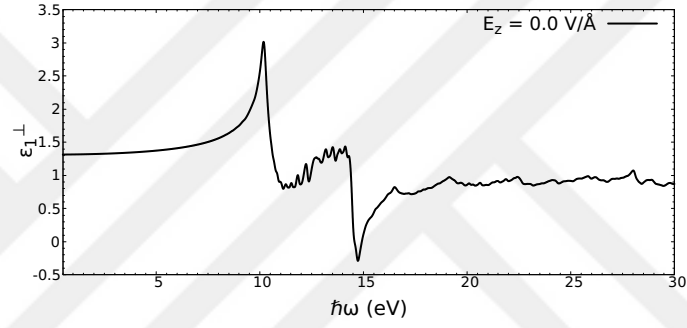
Possible interband transitions corresponding to the optical transitions for monolayer graphene are indicated in Fig. 3.19. Both in electronic band structure and DOS plots, possible transitions are determined such that $\pi \rightarrow \pi^*$ transition is indicated with orange arrow, $\sigma \rightarrow \sigma^*$ transition is indicated with pink arrow,

$\sigma \rightarrow \pi^*$ transition is indicated with brown arrow, and $\pi \rightarrow \sigma^*$ transition is indicated with gray arrow.

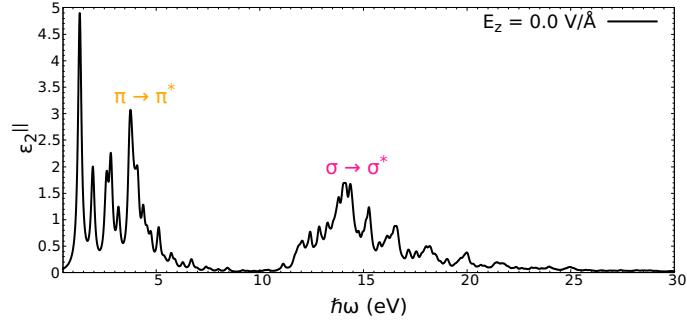
$\varepsilon_2^\perp$ data provides necessary information to determine $\pi \rightarrow \sigma^*$ and $\sigma \rightarrow \pi^*$ transitions whereas $\varepsilon_2^\parallel$ plots indicate $\pi \rightarrow \pi^*$ and $\sigma \rightarrow \sigma^*$ transitions [49, 50]. To investigate the effect of E-field on single-layer graphene, what I am doing is comparing the shifts of the peaks of dielectric function data and matching them with electronic band structures and DOS plots in Chapter 3.1 to deduce possible transitions.



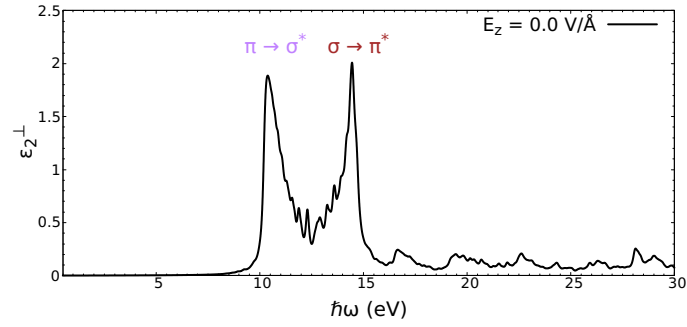
(a)



(b)



(c)



(d)

Figure 3.20: For monolayer graphene without any external field effects: (a) $\varepsilon_1^{\parallel}$ plot. (b) $\varepsilon_1^{\perp}$ plot. (c) $\varepsilon_2^{\parallel}$ plot. (d) $\varepsilon_2^{\perp}$ plot.

In the absence of the E-field, horizontal and perpendicular components of real and imaginary parts of the dielectric function are shown in Fig. 3.20. As in Fig. 3.19, possible optical transitions are indicated as studied in previous articles [49] and [50]. From $\varepsilon_2^{\parallel}$ data in Fig. 3.20c the peak at 3.76 eV corresponds to $\pi \rightarrow \pi^*$ transition whereas the plateau around 14 eV corresponds to $\sigma \rightarrow \sigma^*$ transition. Additionally, the peak at 10.38 eV is corresponding to $\pi \rightarrow \sigma^*$ transition whereas the peak at 14.45 eV corresponds to $\sigma \rightarrow \pi^*$ transition in Fig. 3.20d. Those four transitions are apparent as shown in Fig. 3.19 as well. Notice that for negative values of ε_1 the radiation cannot spread out and negativeness of ε_1 indicates that the corresponding transition is due to plasmons [78]. Therefore, for the single-layer graphene, since ε_1 plots have negative trenches around 4 eV in Fig. 3.20a and around 14.5 eV in Fig. 3.20b, related $\pi \rightarrow \pi^*$ and $\sigma \rightarrow \sigma^*$ transitions are due to plasmons which mean peaks at 3.76 eV in Fig. 3.20c and around 14.5 eV in Fig. 3.20d are plasmonic peaks which are also indicated as such in [79]. Energy region where $\varepsilon_2^{\perp}$ is zero in Fig. 3.20d is a consequence of $\pi \rightarrow \pi^*$ transition being not allowed there which contributes resonance corresponding to the low energy zone [50].

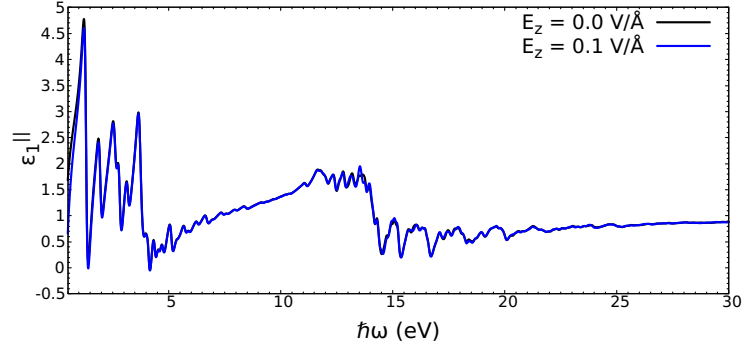
Quantity	P^{thesis} (eV)	P^{others} (eV)
$\varepsilon_2^{\parallel}$	3.76	4.0 ^[80] , 4.0 ^[49] , 4.14 ^[81] , 4.77 ^[82]
$\varepsilon_2^{\parallel}$	14	14.49 ^[80] , 14.0 ^[49]
$\varepsilon_2^{\perp}$	10.38	11.0 ^[49] , 11 ^[81]
$\varepsilon_2^{\perp}$	14.45	14.0 ^[49] , 14 ^[81]

Table 3.2: Comparison of the positions of the peaks corresponding to $\varepsilon_2^{\parallel}$ and $\varepsilon_2^{\perp}$ for monolayer graphene calculated in this thesis from Fig. 3.20c & Fig. 3.20d with cited articles.

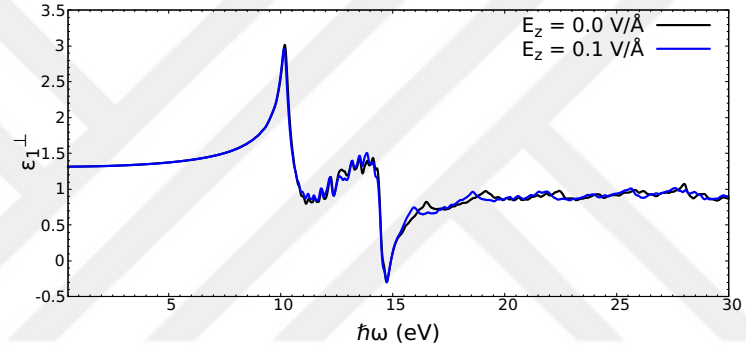
In Table 3.2, P^{thesis} represents the peak positions corresponding to $\varepsilon_2^{\parallel}$ and $\varepsilon_2^{\perp}$ for monolayer graphene calculated in this thesis whereas P^{others} stands for those obtained in cited articles. P^{thesis} for $\varepsilon_2^{\parallel}$ might be regarded as in accordance with

[49], [80], and [81]. There is a slight difference with data in [82] that might be caused by the interaction between p_z orbitals and silicon carbide & single-layer graphene complex since Chen et al. transferred single-layer graphene on silicon carbide. P^{thesis} values for $\varepsilon_2^\perp$ which are at 10.38 eV and 14.45 eV are slightly different than those calculated in [49] and [81]. Differences between the calculations might be caused due to the variations in calculation parameters involving k-mesh sampling in the fBZ, the type of pseudopotential used for describing carbon atoms, kinetic energy cutoff, and smearing.

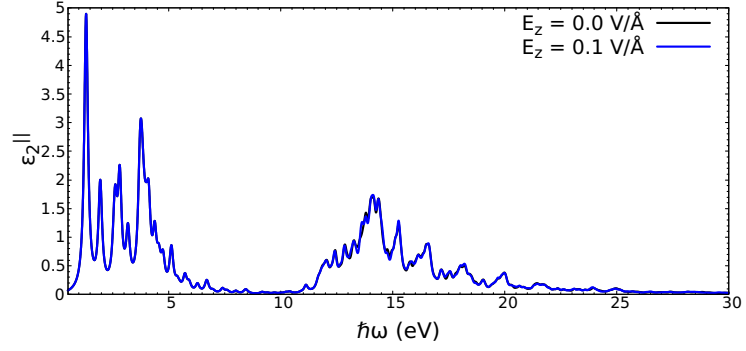
For completeness, ε_1 plots are included. As mentioned previously, transitions are apparently understood by $\varepsilon_2^\parallel$ and $\varepsilon_2^\perp$ data. From Fig. 3.21c to Fig. 3.36c, $\varepsilon_2^\parallel$ curves corresponding to E-field and no-E-field cases are almost identical which are tabulated in Table 3.4. It may be seen with ease from Table 3.4 that up to 2.5 V/Å E-field amplitude, peaks P4 and P5 are not changed drastically which correspond to $\pi \rightarrow \pi^*$ and $\sigma \rightarrow \sigma^*$ transitions, respectively. Therefore, those two transitions continue to take place around the same places. Starting from Fig. 3.25c corresponding to $E_z=0.5$ V/Å, the amplitude of the peak at 1.32 eV started to decrease after $E_z=0.5$ V/Å. For instance, its amplitude is 4.88 for no-E-field case whereas its amplitude for $E_z=2.2$ V/Å is 0.24, and 0.11 for $E_z=2.5$ V/Å. Another considerable decrease is observed at 1.95 eV and this decrease started to be apparent after Fig. 3.27c corresponding to $E_z=0.7$ V/Å external field. The amplitude of the corresponding peak is 2.00 for no-E-field case and it is decreased to 1.97 for $E_z=0.7$ V/Å, and became 0.71 for $E_z=2.5$ V/Å. The peaks at 2.62 eV and 2.81 eV slightly decreased as well and became kind of noticeable after Fig. 3.34c corresponding to $E_z=2.0$ V/Å. For the no-E-field case, amplitudes of those peaks were 1.93 and 2.26, respectively and they decreased to 1.68 and 2.13 for $E_z=2.5$ V/Å, respectively. However, the decreases corresponding to the last two peaks are not significant.



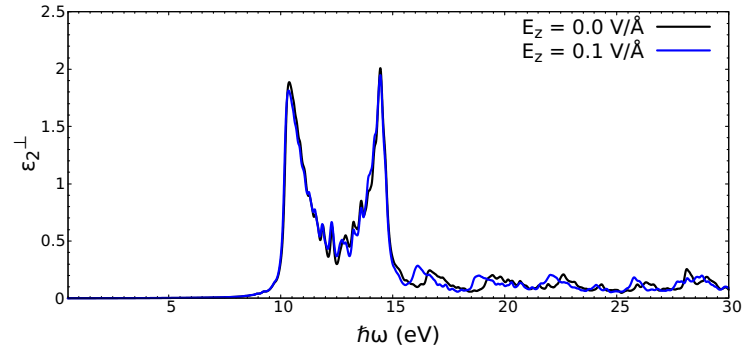
(a)



(b)

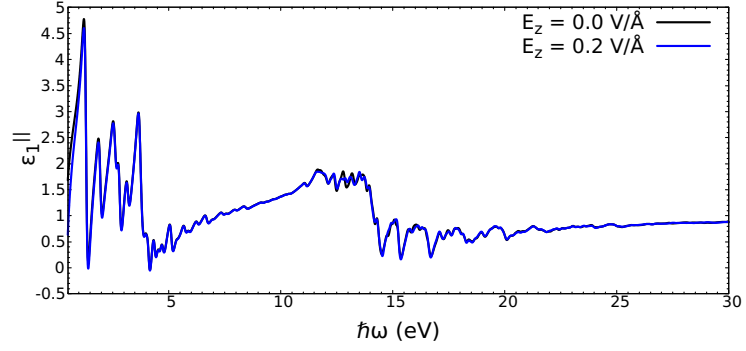


(c)

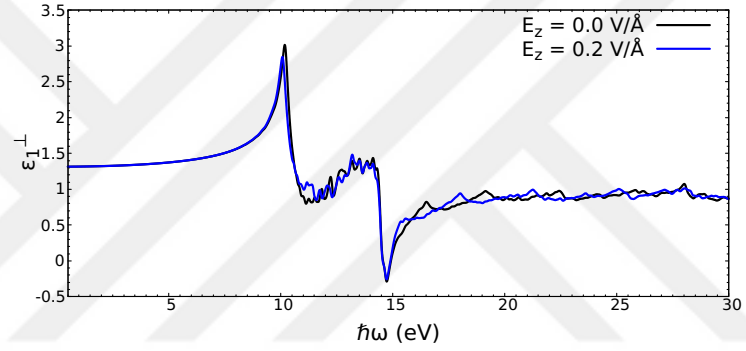


(d)

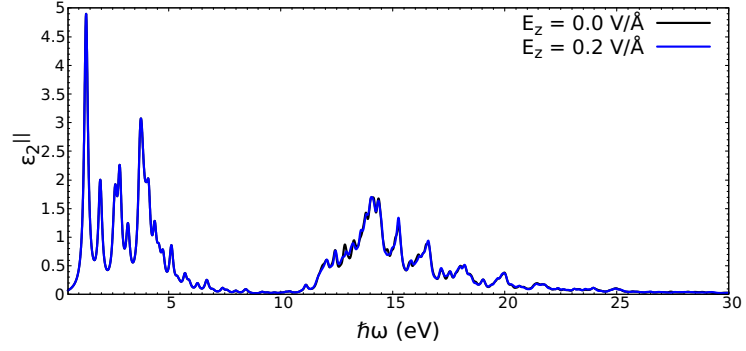
Figure 3.21: Dielectric function data under the influence of an E-field of magnitude $E_z=0.1$ V/Å: (a) $\varepsilon_1^{\parallel}$ plot. (b) $\varepsilon_1^{\perp}$ plot. (c) $\varepsilon_2^{\parallel}$ plot. (d) $\varepsilon_2^{\perp}$ plot.



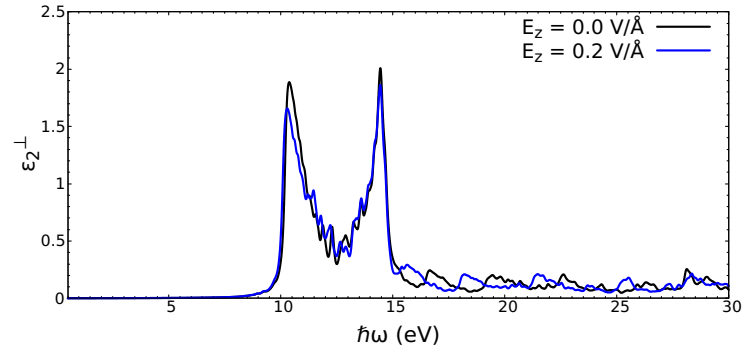
(a)



(b)

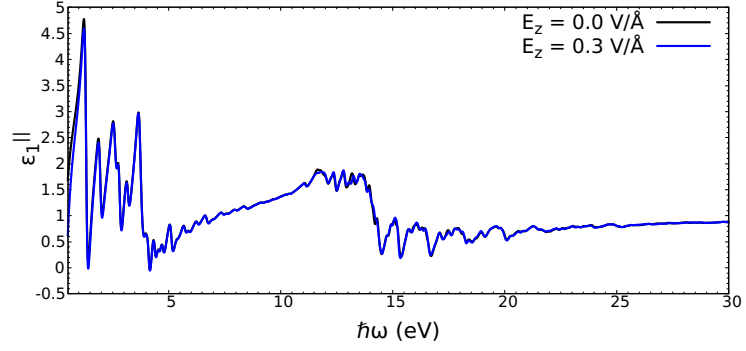


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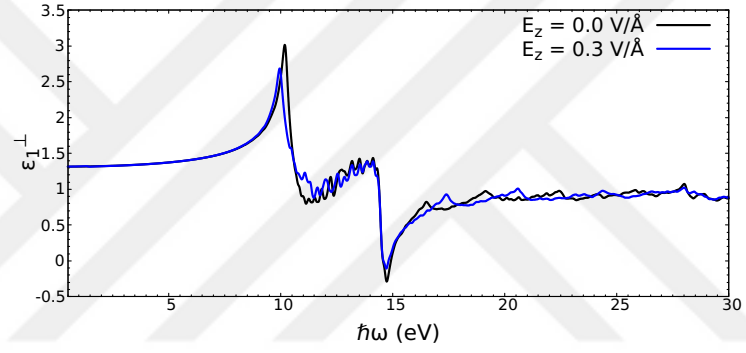


(d)

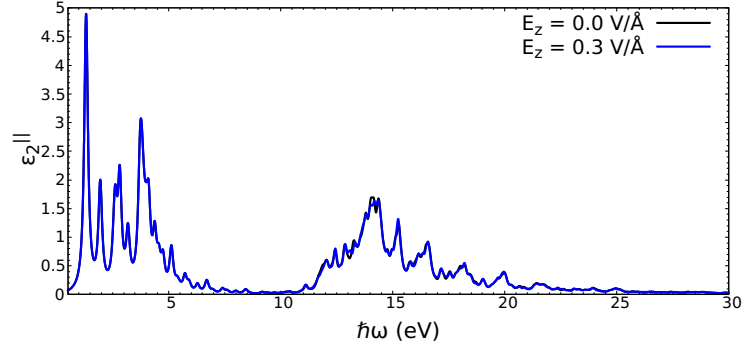
Figure 3.22: Dielectric function data under the perpendicular electric field of amplitude $E_z=0.2$ V/Å: (a) $\varepsilon_1^{\parallel}$ plot. (b) $\varepsilon_1^{\perp}$ plot. (c) $\varepsilon_2^{\parallel}$ plot. (d) $\varepsilon_2^{\perp}$ plot.



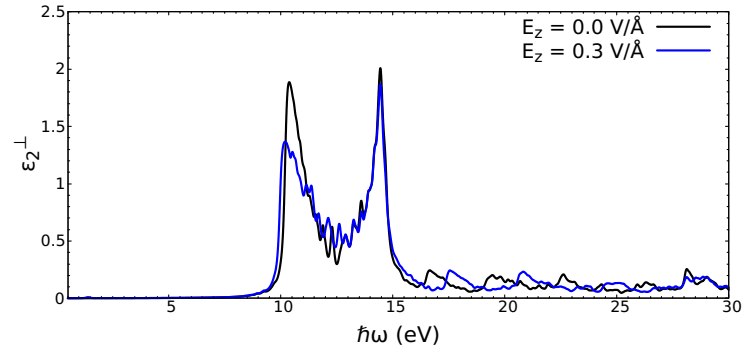
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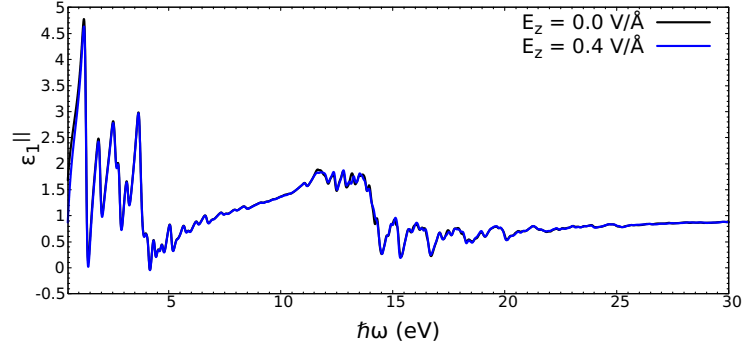


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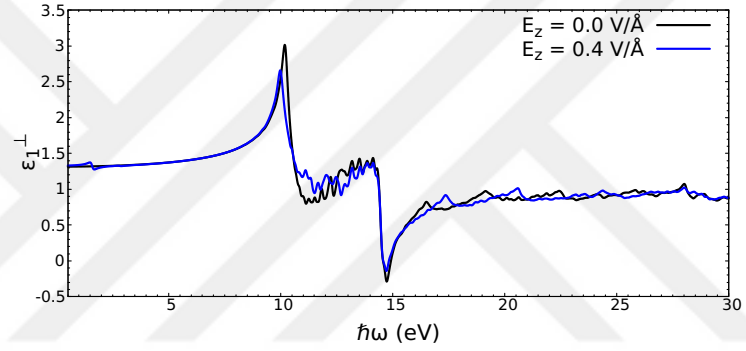


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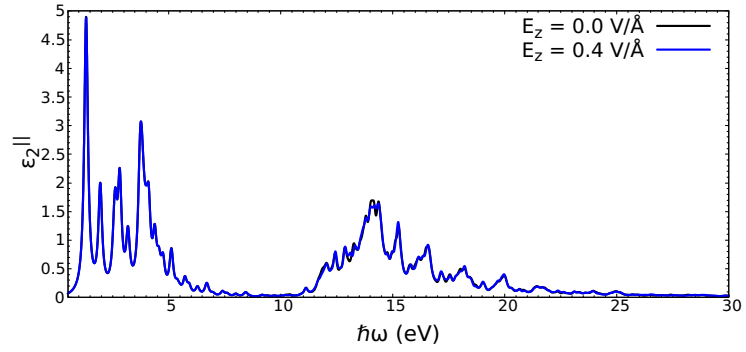
Figure 3.23: Dielectric function data under $E_z=0.3 \text{ V/\AA}$: (a) $\varepsilon_1^{\parallel}$ plot. (b) $\varepsilon_1^{\perp}$ plot. (c) $\varepsilon_2^{\parallel}$ plot. (d) $\varepsilon_2^{\perp}$ plot.



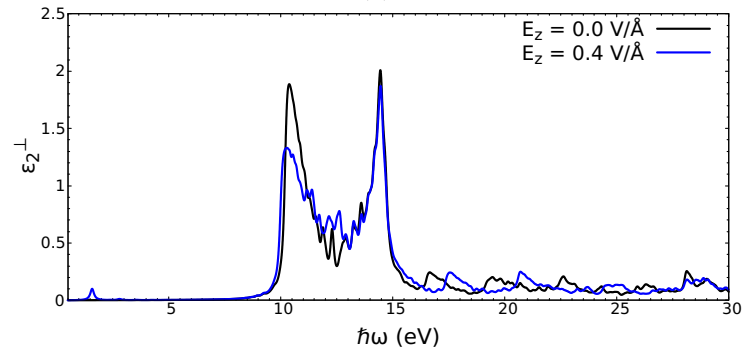
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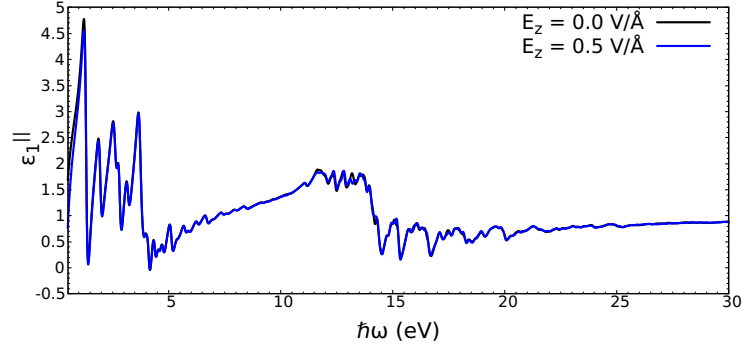


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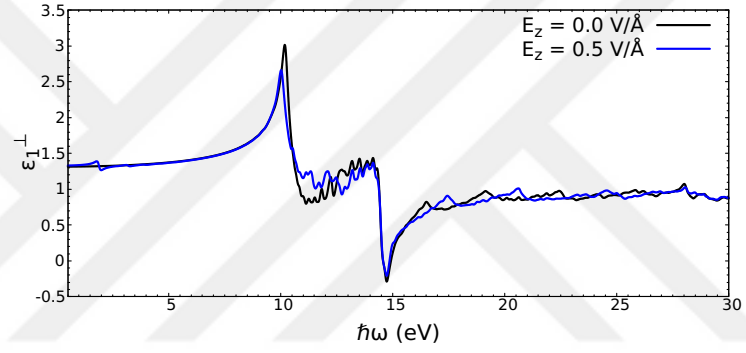


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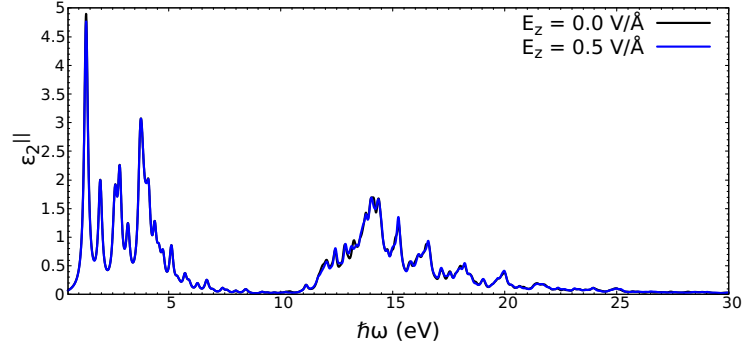
Figure 3.24: Dielectric function data in the presence of an E-field of magnitude $E_z=0.4$ V/Å: (a) $\epsilon_1^{\parallel}$ plot. (b) $\epsilon_1^{\perp}$ plot. (c) $\epsilon_2^{\parallel}$ plot. (d) $\epsilon_2^{\perp}$ plot.



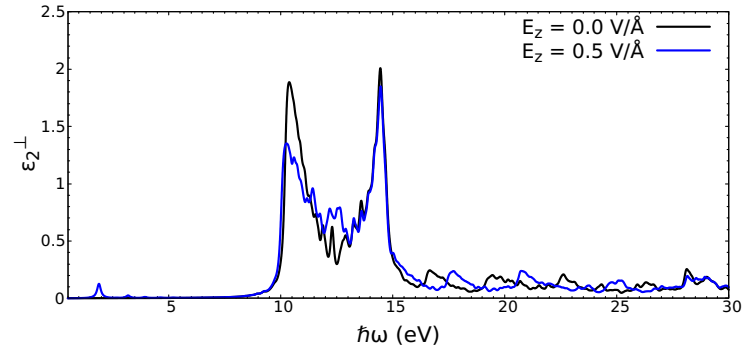
(a)



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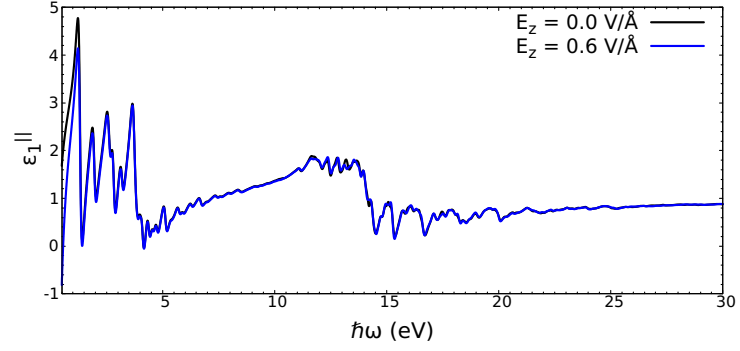


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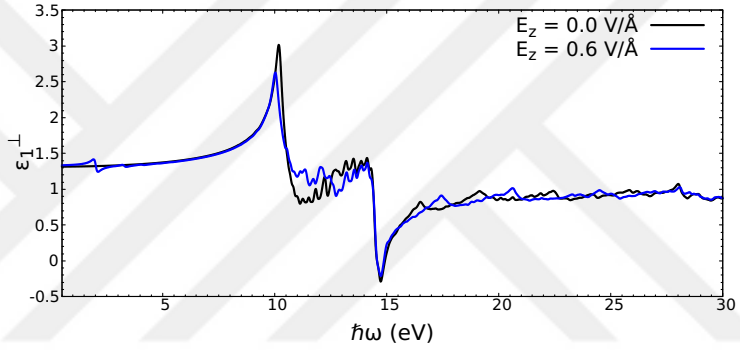


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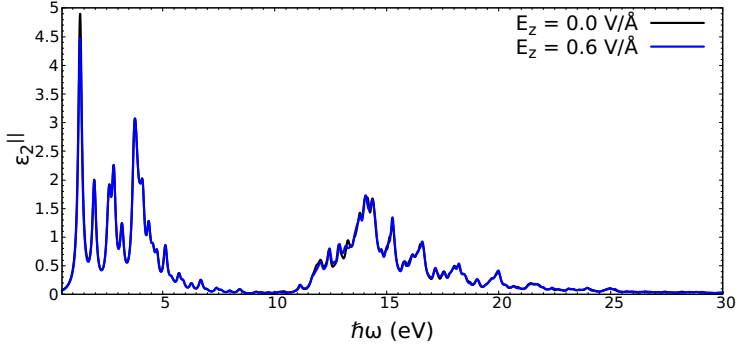
Figure 3.25: Dielectric function data under $E_z=0.5$ V/Å: (a) $\varepsilon_1^{\parallel}$ plot. (b) $\varepsilon_1^{\perp}$ plot. (c) $\varepsilon_2^{\parallel}$ plot. (d) $\varepsilon_2^{\perp}$ plot.



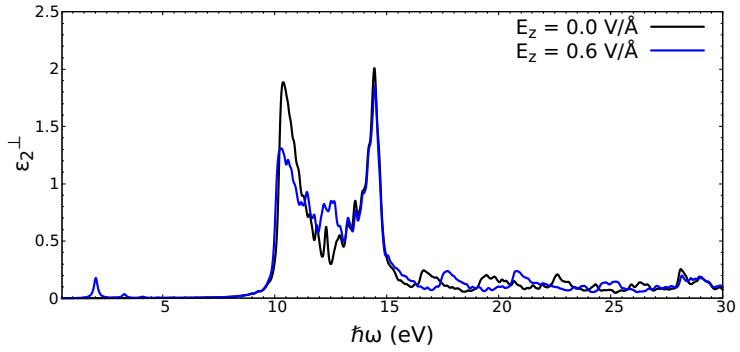
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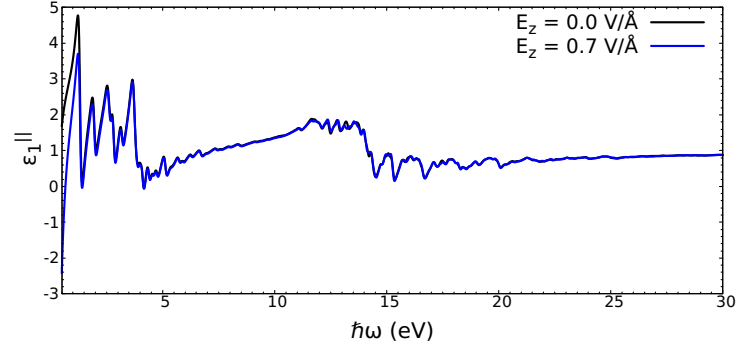


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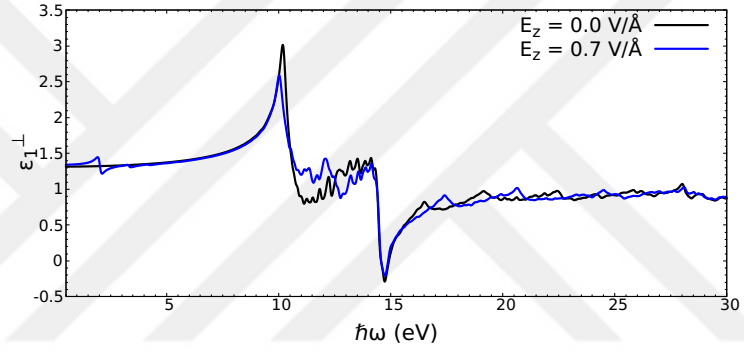


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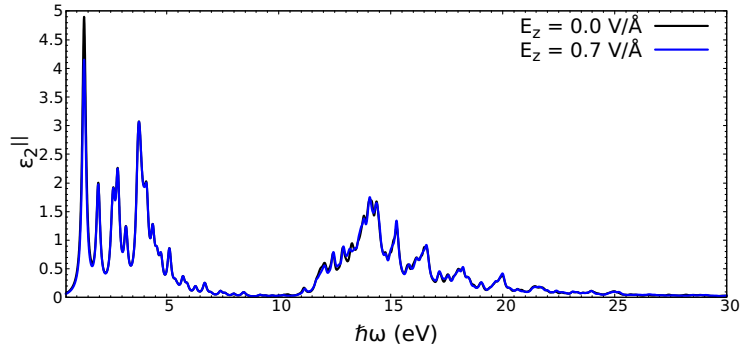
Figure 3.26: Dielectric function data under the influence of an E-field magnitude of $E_z=0.6$ V/Å: (a) $\varepsilon_1^{\parallel}$ plot. (b) $\varepsilon_1^{\perp}$ plot. (c) $\varepsilon_2^{\parallel}$ plot. (d) $\varepsilon_2^{\perp}$ plot.



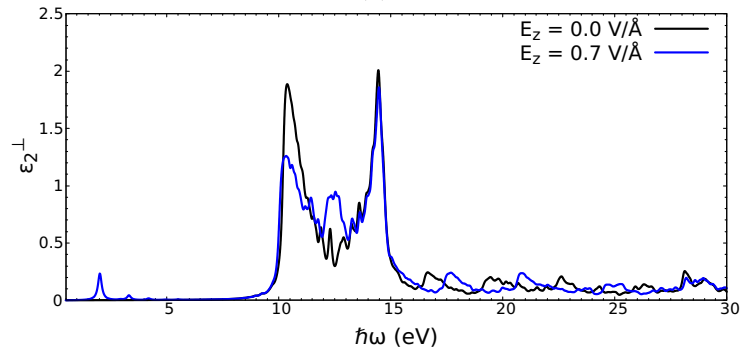
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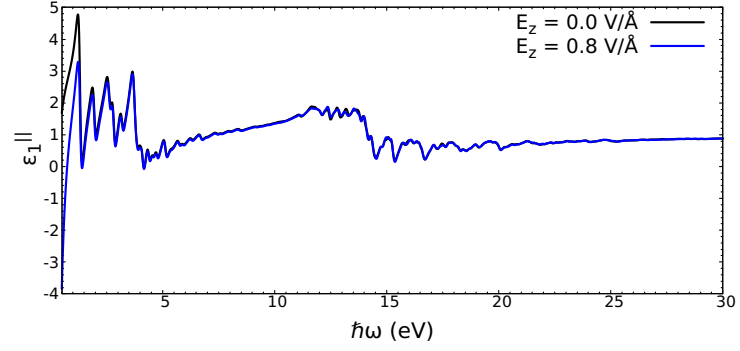


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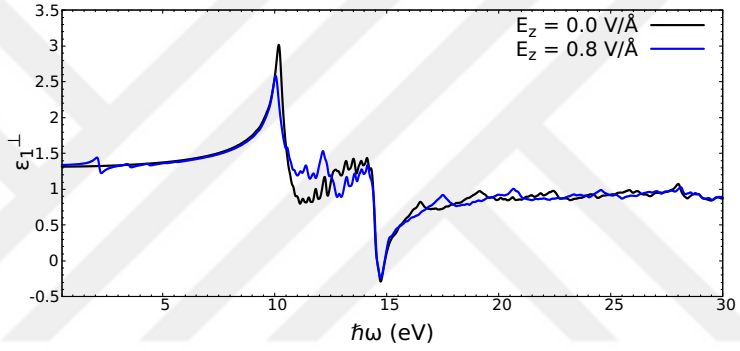


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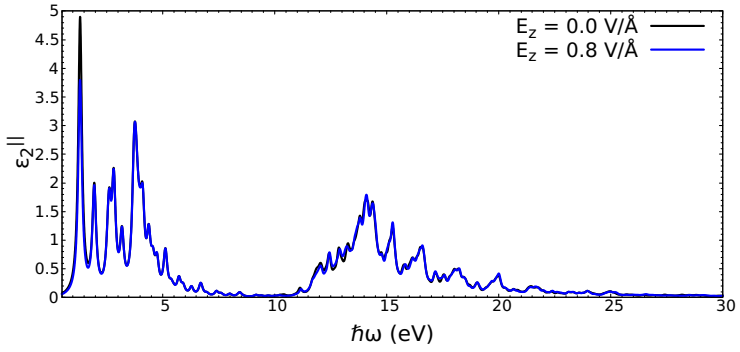
Figure 3.27: Dielectric function data under $E_z=0.7$ V/Å: (a) $\varepsilon_1^{\parallel}$ plot. (b) $\varepsilon_1^{\perp}$ plot. (c) $\varepsilon_2^{\parallel}$ plot. (d) $\varepsilon_2^{\perp}$ plot.



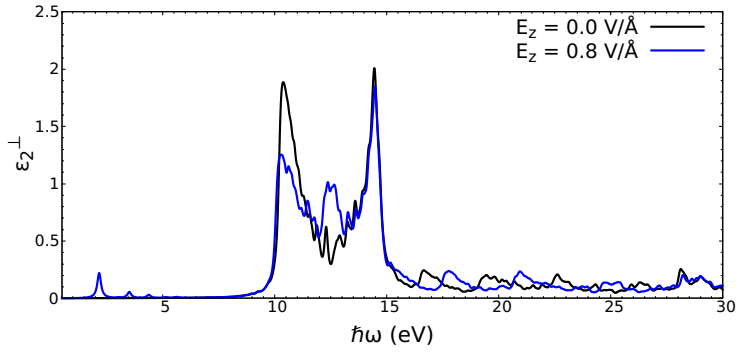
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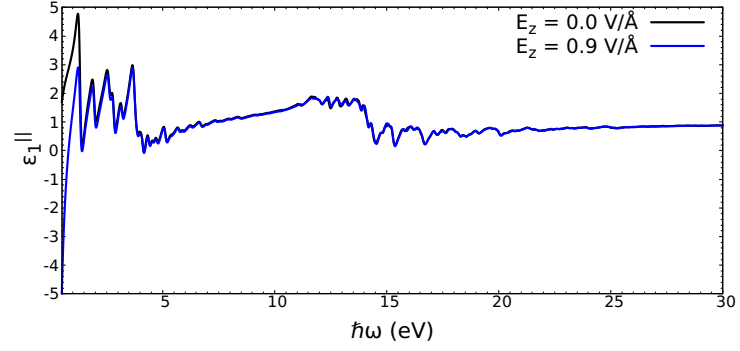


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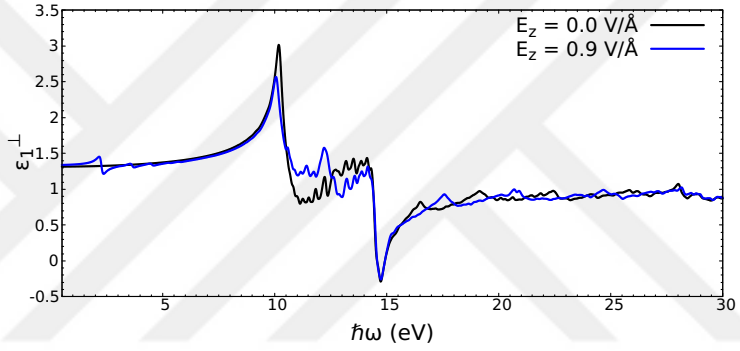


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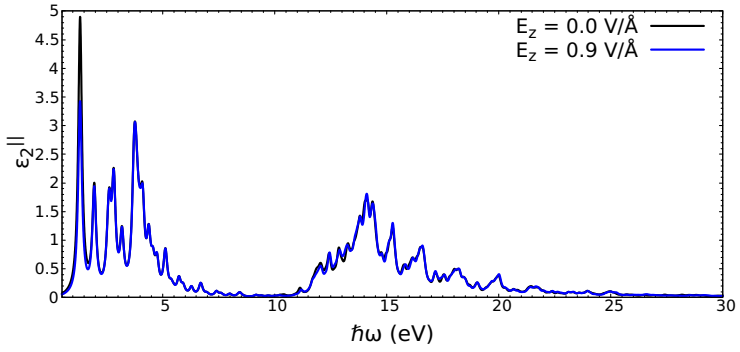
Figure 3.28: Dielectric function data under the influence of an E-field of magnitude $E_z=0.8$ V/Å: (a) $\varepsilon_1^{\parallel}$ plot. (b) $\varepsilon_1^{\perp}$ plot. (c) $\varepsilon_2^{\parallel}$ plot. (d) $\varepsilon_2^{\perp}$ plot.



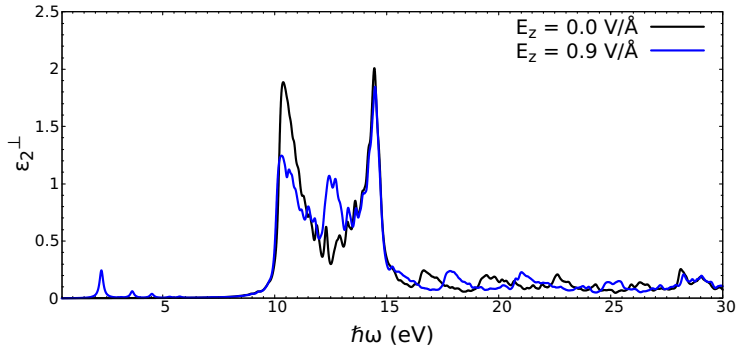
(a)



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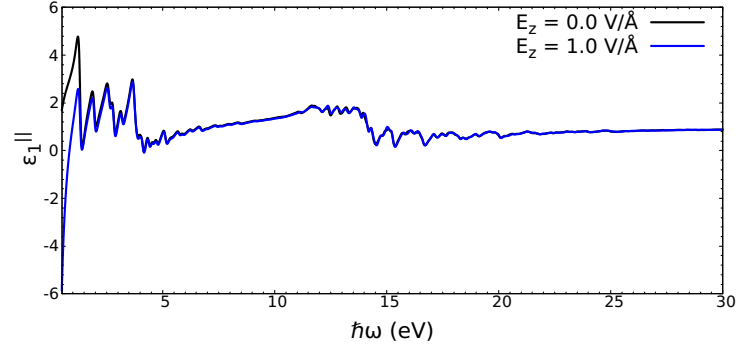


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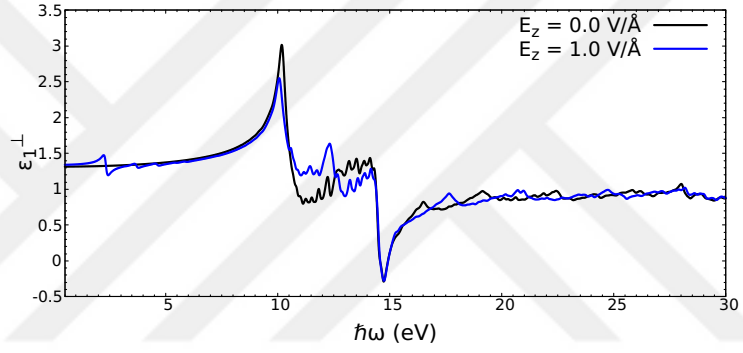


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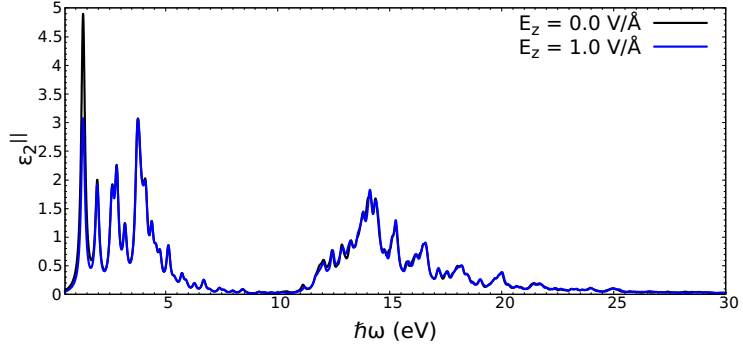
Figure 3.29: Dielectric function data under the influence of an E-field of magnitude $E_z=0.9$ V/Å: (a) $\varepsilon_1^{\parallel}$ plot. (b) $\varepsilon_1^{\perp}$ plot. (c) $\varepsilon_2^{\parallel}$ plot. (d) $\varepsilon_2^{\perp}$ plot.



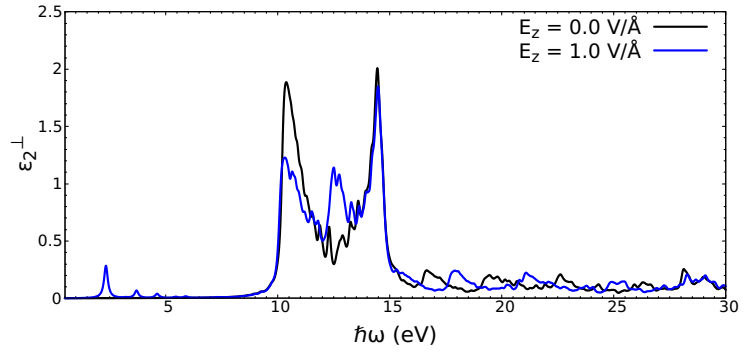
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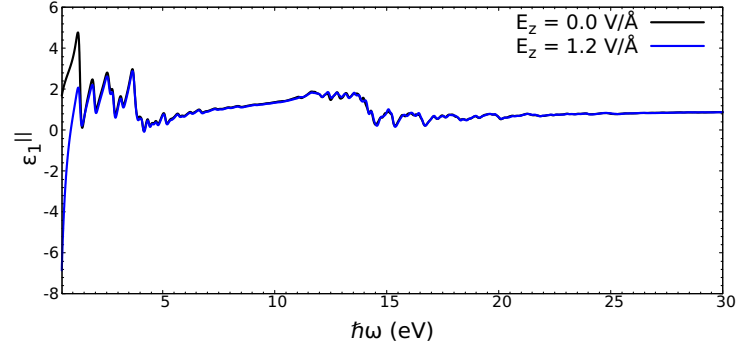


(c)

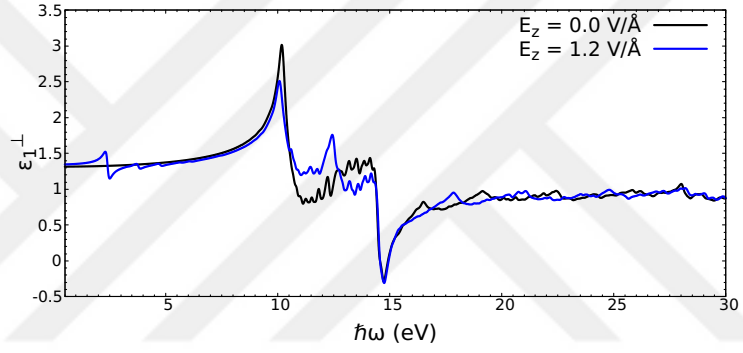


(d)

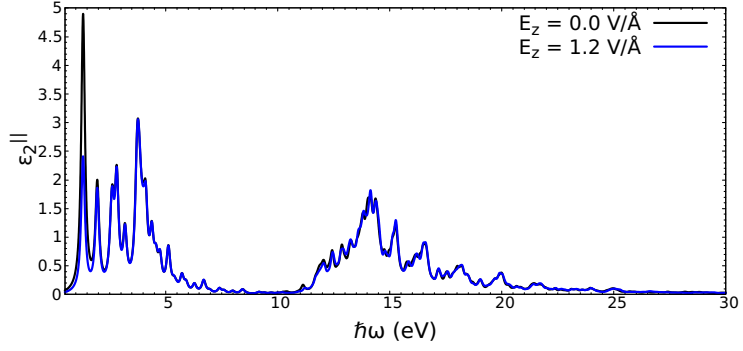
Figure 3.30: Dielectric function data under $E_z=1.0$ V/Å: (a) $\varepsilon_1^{\parallel}$ plot. (b) $\varepsilon_1^{\perp}$ plot. (c) $\varepsilon_2^{\parallel}$ plot. (d) $\varepsilon_2^{\perp}$ plot.



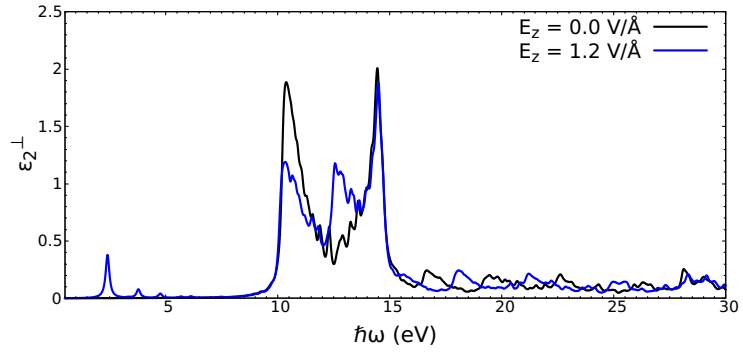
(a)



(b)

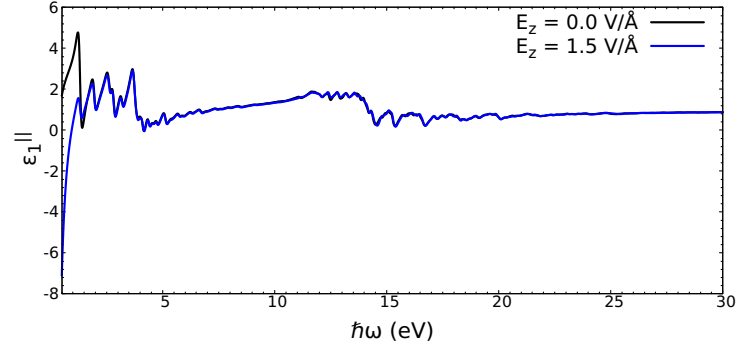


(c)

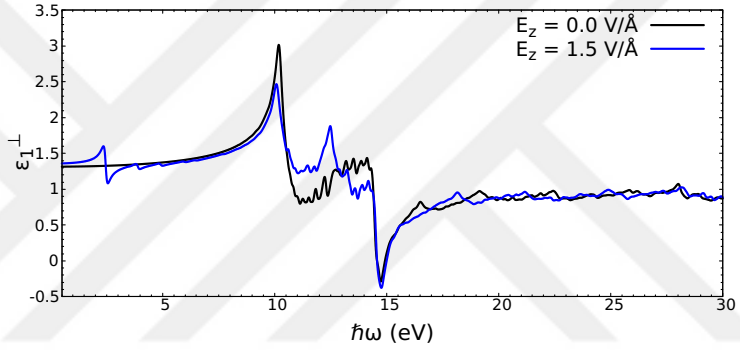


(d)

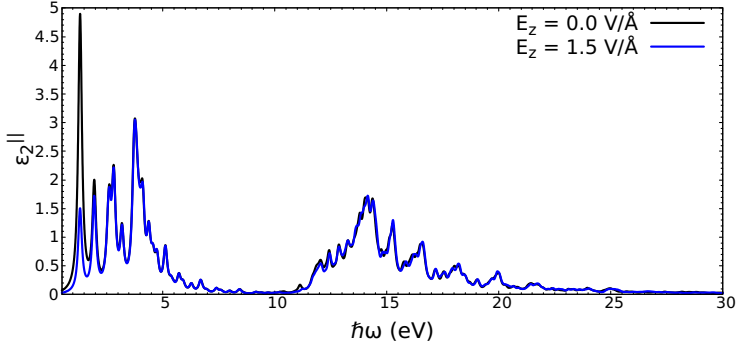
Figure 3.31: Dielectric function data under an E-field of magnitude $E_z=1.2 \text{ V/\AA}$: (a) $\epsilon_1^{\parallel}$ plot. (b) $\epsilon_1^{\perp}$ plot. (c) $\epsilon_2^{\parallel}$ plot. (d) $\epsilon_2^{\perp}$ plot.



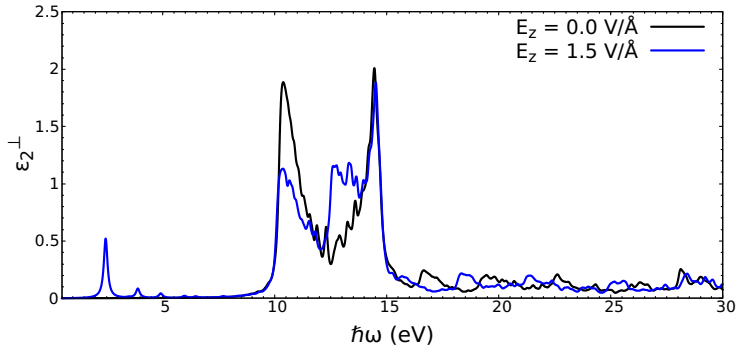
(a)



(b)

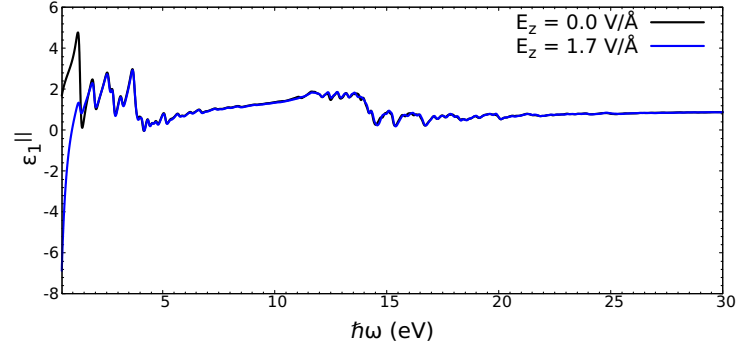


(c)

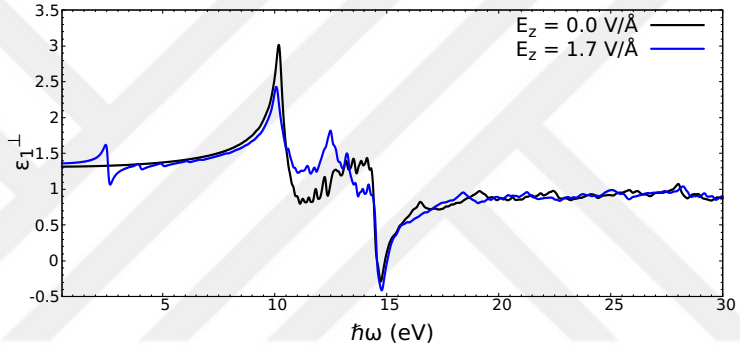


(d)

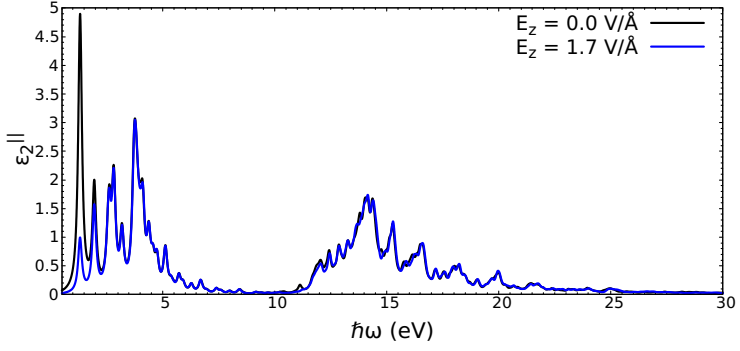
Figure 3.32: Dielectric function data under $E_z=1.5$ V/Å: (a) $\varepsilon_1^{\parallel}$ plot. (b) $\varepsilon_1^{\perp}$ plot. (c) $\varepsilon_2^{\parallel}$ plot. (d) $\varepsilon_2^{\perp}$ plot.



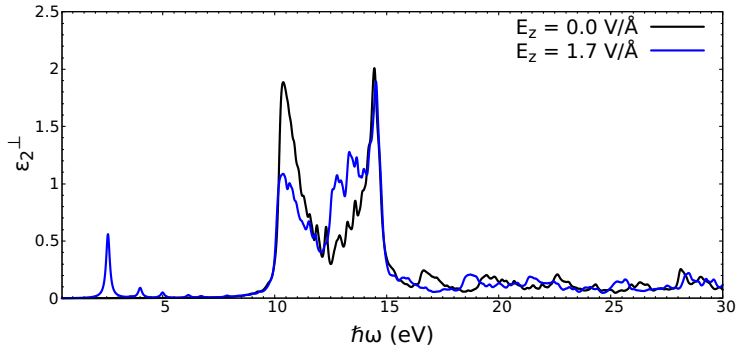
(a)



(b)

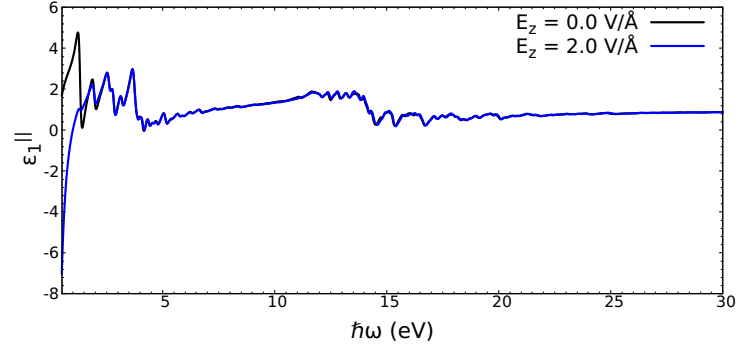


(c)

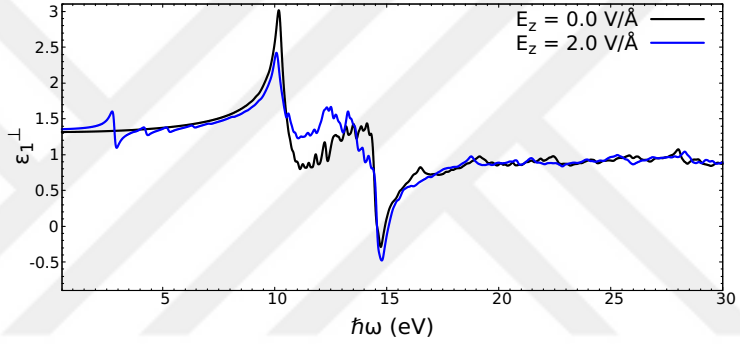


(d)

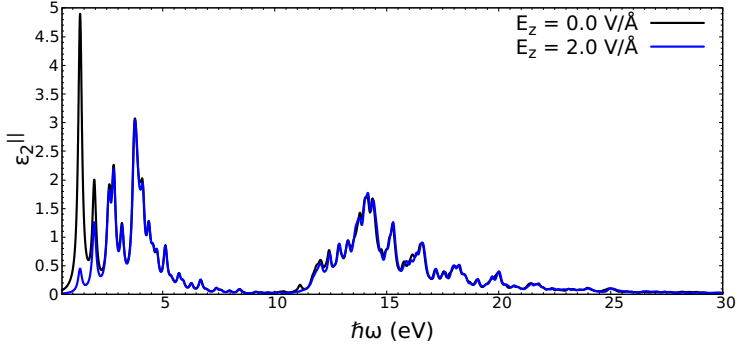
Figure 3.33: Dielectric function data when the strength of applied perpendicular electric field is $E_z=1.7$ V/Å: (a) $\varepsilon_1^{\parallel}$ plot. (b) $\varepsilon_1^{\perp}$ plot. (c) $\varepsilon_2^{\parallel}$ plot. (d) $\varepsilon_2^{\perp}$ plot.



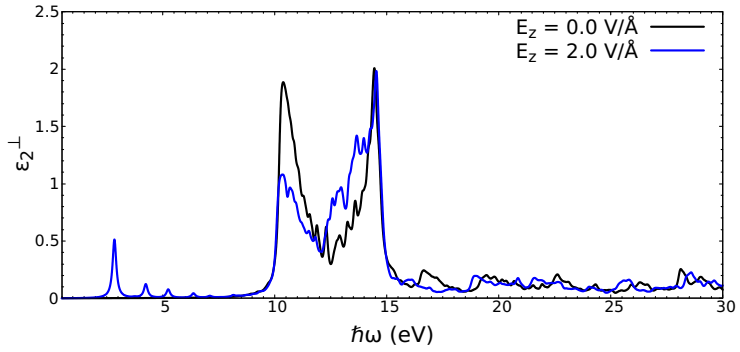
(a)



(b)

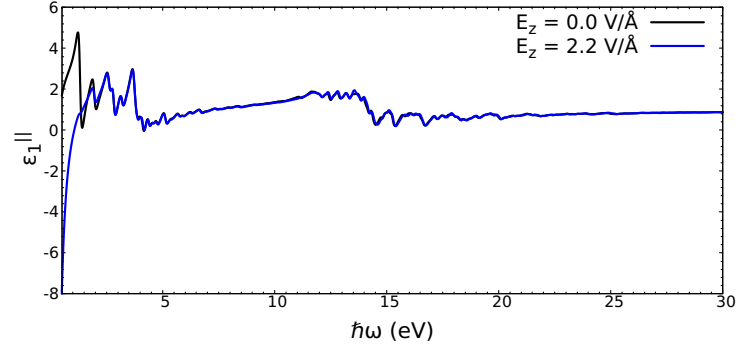


(c)

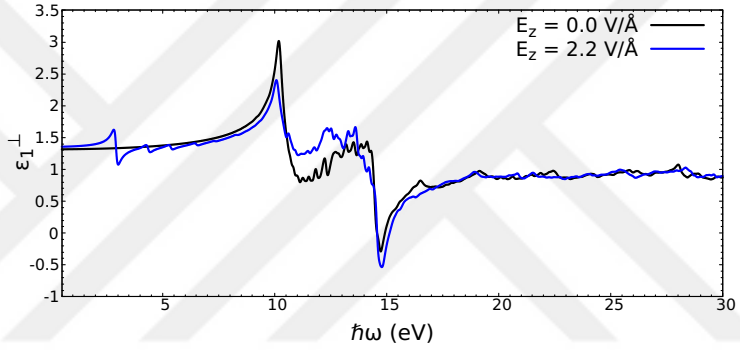


(d)

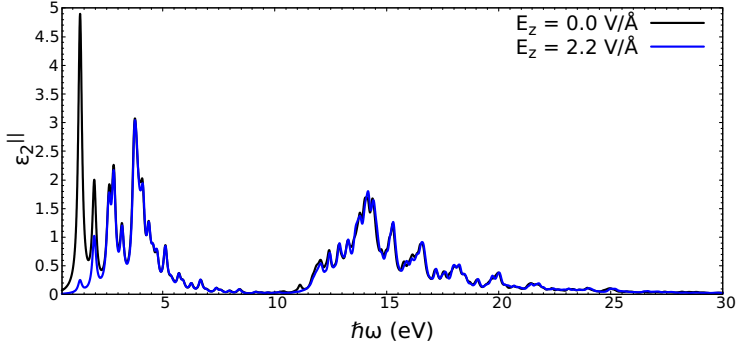
Figure 3.34: Dielectric function data in the presence of an E-field of magnitude $E_z=2.0$ V/Å: (a) $\epsilon_1^{\parallel}$ plot. (b) $\epsilon_1^{\perp}$ plot. (c) $\epsilon_2^{\parallel}$ plot. (d) $\epsilon_2^{\perp}$ plot.



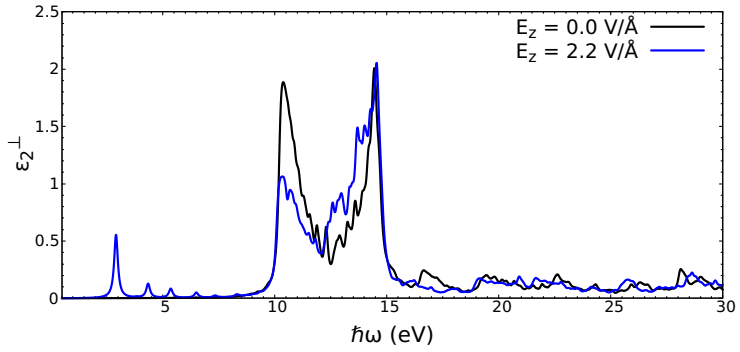
(a)



(b)

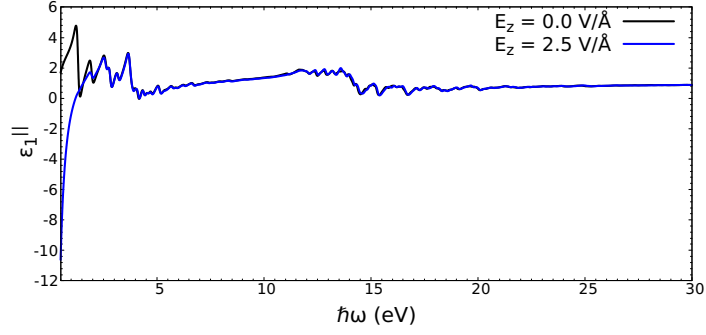


(c)

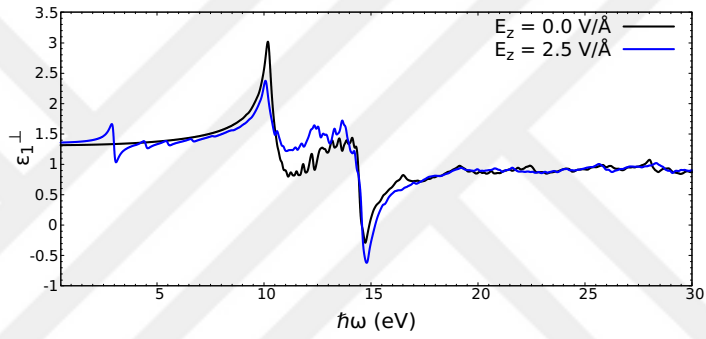


(d)

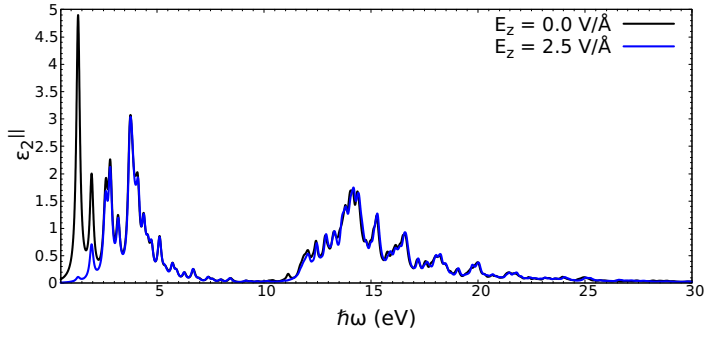
Figure 3.35: Dielectric function data under the influence of an E-field of magnitude $E_z=2.2$ V/Å: (a) $\epsilon_1^{\parallel}$ plot. (b) $\epsilon_1^{\perp}$ plot. (c) $\epsilon_2^{\parallel}$ plot. (d) $\epsilon_2^{\perp}$ plot.



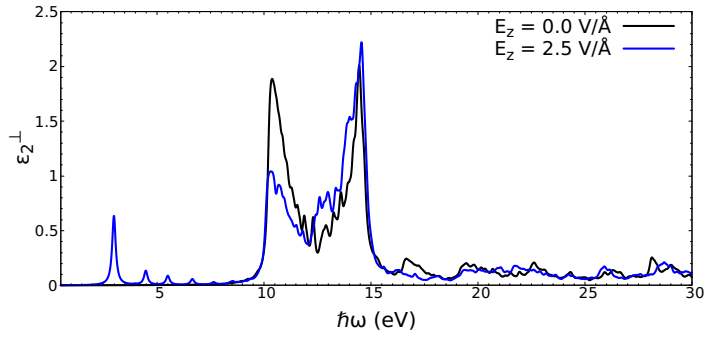
(a)



(b)



(c)



(d)

Figure 3.36: Dielectric function data under the influence of a perpendicular electric field of magnitude $E_z=2.5$ V/Å: (a) $\varepsilon_1^{\parallel}$ plot. (b) $\varepsilon_1^{\perp}$ plot. (c) $\varepsilon_2^{\parallel}$ plot. (d) $\varepsilon_2^{\perp}$ plot.

Even for $E_z=0.1$ V/Å, considerable changes started to be apparent for $\varepsilon_2^\perp$ which makes sense since the E-field is along vertical direction to the graphene sheet and $\varepsilon_2^\perp$ is describing the direction of polarization that is perpendicular to the graphene sheet as well. Transitions corresponding to $\varepsilon_2^\perp$ plots are $\pi \rightarrow \sigma^*$ at 10.5 eV, and $\sigma \rightarrow \pi^*$ at 14.5 eV for no-E-field case as indicated in Fig. 3.20d. Let me start by considering low energy zone first, between 0 eV and 10 eV for $\varepsilon_2^\perp$ plots. Starting from Fig. 3.22d for $E_z=0.2$ V/Å, the peak at 10.37 eV redshifts to 10.29 eV and this redshift is observed for E-field amplitudes $0.2 \text{ V/Å} \leq E_z \leq 1.0 \text{ V/Å}$ and observed the strongest when $E_z=0.3$ V/Å which is shifted to 10.17 eV. In addition to this, as the E-field is introduced to the system, amplitude of the last cited peak started to decrease for all E-field amplitudes applied. Including Fig. 3.24d corresponding to $E_z=0.4$ V/Å, new peak structures are observed in the low energy zone.

E_z (V/Å)	P1 (eV)	A1	P2 (eV)	A2	P3 (eV)	A3	P4 (eV)	A4	P5 (eV)	A5	P6 (eV)	A6	P7 (eV)	A7
0.4	1.58	0.10	-	-	-	-	-	-	-	-	-	-	-	-
0.5	1.89	0.13	3.19	0.025	3.94	0.012	4.63	0.0074	5.21	0.0065	-	-	-	-
0.6	2.02	0.17	3.29	0.037	4.11	0.014	4.81	0.0069	5.40	0.0066	-	-	-	-
0.7	2.02	0.23	2.95	0.012	3.32	0.044	4.19	0.016	4.95	0.0066	5.52	0.0078	-	-
0.8	2.17	0.22	3.05	0.011	3.51	0.056	4.38	0.031	5.15	0.011	5.63	0.012	-	-
0.9	2.27	0.24	3.14	0.011	3.64	0.062	4.52	0.039	5.31	0.014	5.76	0.015	7.22	0.0096
1.0	2.34	0.29	3.22	0.012	3.70	0.068	4.62	0.040	5.45	0.014	5.89	0.017	7.31	0.011
1.2	2.41	0.38	3.34	0.014	3.78	0.079	4.76	0.042	5.69	0.016	6.13	0.017	7.47	0.014
1.5	2.46	0.52	3.50	0.017	3.89	0.086	4.92	0.044	5.97	0.022	6.47	0.017	7.70	0.019
1.7	2.56	0.56	3.59	0.019	3.99	0.092	4.99	0.051	6.15	0.029	6.72	0.019	7.88	0.024
2.0	2.85	0.51	3.76	0.018	4.25	0.13	5.25	0.078	6.38	0.044	7.10	0.022	8.15	0.029
2.2	2.92	0.55	3.85	0.018	4.35	0.13	5.36	0.085	6.49	0.051	7.34	0.025	8.32	0.036
2.5	2.99	0.64	3.98	0.018	4.47	0.14	5.51	0.088	6.65	0.058	7.65	0.031	8.53	0.040

Table 3.3: Position of peaks (P) and their amplitudes (A) between 0 eV and 10 eV for the E-field magnitudes $0.4 \text{ V/Å} \leq E_z \leq 2.5 \text{ V/Å}$ corresponding to $\varepsilon_2^\perp$ plots from Fig. 3.24d to Fig. 3.36d.

In Table 3.3, number of new peaks (up to 7 peaks) appeared due to the E-field, position of the peaks (denoted as P) and amplitude of them (denoted as A) are given. P_j represents the position of j^{th} peak on the energy axis whereas A_j stands for the amplitude of peak j for $j = 1, 2, \dots, 7$ such that j is the number of peaks. Corresponding data are taken from Fig. 3.24d to Fig. 3.36d. The boxes containing no numbers mean there are no peaks observed. Each additional peak corresponds to an interband transition that is a consequence of the introduced E-field.

Tables 3.4, 3.5, 3.6, 3.7, are tabulated by considering visible peaks between 0 eV and 16.50 eV, i.e., the peaks that do not require to zoom-in to be detected, corresponding to both planar and vertical components for ε_1 and ε_2 . They are compared with no-E-case and they will be helpful for determining interband transitions after comparison with related DOS and electronic band structure data.

As indicated in Table 3.7, in low energy zone for $0.1 \text{ V/\AA} \leq E_z \leq 0.3 \text{ V/\AA}$, no additional peaks have been observed. I start analysis with Table 3.7 that shows P and A information corresponding to the $\varepsilon_2^\perp$ between 0 eV and 16 eV for all E-field magnitudes and no-E-case. For $0.0 \text{ V/\AA} \leq E_z \leq 0.2 \text{ V/\AA}$ there are two main peaks denoted by P4 and P6. As described previously, in the case of $E_z = 0.0 \text{ V/\AA}$, P4 corresponds to $\pi \rightarrow \sigma^*$ transition whereas P6 is due to $\sigma \rightarrow \pi^*$ transition. Under the influence of E-field, those peaks shifted and new peaks appeared. After comparison with the DOS and electronic band structure plots corresponding to $0.0 \text{ V/\AA} \leq E_z \leq 0.2 \text{ V/\AA}$, P4 corresponds to $\pi \rightarrow \sigma^*$ transition, P6 corresponds to $\sigma \rightarrow \pi^*$ transition as expected since those are shifted versions of the peaks corresponding to above cited transitions.

When the amplitude of E-field is $0.1 \text{ V/\AA}$, $\pi \rightarrow \sigma^*$ transition takes place from -6.56 eV towards 3.79 eV. $\sigma \rightarrow \pi^*$ transition occurs from -13.11 eV to 1.34 eV. Both of two cited transitions are observed between Γ and K points in the fBZ.

For $E_z = 0.2 \text{ V/\AA}$, $\pi \rightarrow \sigma^*$ transition is from -7.51 eV to 2.78 eV around the Γ point whereas $\sigma \rightarrow \pi^*$ transition takes place between Γ and K points in the FBZ from -12.36 eV towards 2.09 eV.

E_z (V/\AA)	P1 (eV)	A1	P2 (eV)	A2	P3 (eV)	A3	P4 (eV)	A4	P5 (eV)	A5	P6 (eV)	A6	P7 (eV)	A7
0.0	1.22	4.77	1.86	2.48	2.53	2.82	3.65	2.98	11.65	1.88	15.07	0.93	16.05	0.83
0.1	1.22	4.61	1.87	2.41	2.53	2.77	3.65	2.97	13.54	1.95	15.08	0.95	16.06	0.82
0.2	1.22	4.60	1.87	2.41	2.53	2.77	3.65	2.96	11.64	1.85	15.16	0.93	16.13	0.81
0.3	1.22	4.60	1.87	2.41	2.53	2.77	3.65	2.96	12.81	1.87	15.11	0.96	16.07	0.87
0.4	1.22	4.63	1.87	2.42	2.53	2.78	3.65	2.97	12.81	1.87	15.12	0.96	16.07	0.87
0.5	1.22	4.55	1.87	2.43	2.52	2.78	3.65	2.97	12.82	1.86	15.17	0.94	16.07	0.86
0.6	1.22	4.14	1.87	2.37	2.52	2.74	3.65	2.95	12.37	1.86	15.18	0.92	16.07	0.85
0.7	1.22	3.71	1.87	2.29	2.52	2.69	3.66	2.92	12.37	1.87	15.18	0.91	16.07	0.85
0.8	1.23	3.29	1.87	2.25	2.52	2.66	3.66	2.91	12.37	1.87	14.98	0.92	16.07	0.84
0.9	1.23	2.91	1.87	2.22	2.52	2.63	3.66	2.89	12.37	1.88	15.01	0.95	16.07	0.85
1.0	1.23	2.58	1.87	2.21	2.52	2.62	3.66	2.88	12.37	1.88	15.03	0.99	16.08	0.85
1.2	1.24	2.08	1.87	2.22	2.52	2.62	3.66	2.88	12.37	1.86	15.08	1.02	16.10	0.85
1.5	1.24	1.57	1.87	2.28	2.52	2.68	3.66	2.91	12.37	1.86	15.09	0.97	16.14	0.85
1.7	1.25	1.34	1.87	2.30	2.52	2.74	3.66	2.93	12.79	1.86	15.10	0.95	16.16	0.85
2.0	1.27	1.04	1.87	2.22	2.52	2.79	3.66	2.96	13.55	1.89	15.11	0.95	16.25	0.84
2.2	-	-	1.87	2.05	2.52	2.77	3.66	2.96	13.55	1.95	15.11	0.97	16.30	0.81
2.5	-	-	1.88	1.71	2.52	2.67	3.66	2.93	13.58	1.98	15.12	0.97	16.08	0.81

Table 3.4: Position of peaks and their amplitudes between 0 eV and 16.50 eV for the E-field magnitudes $0.0 \text{ V/\AA} \leq E_z \leq 2.5 \text{ V/\AA}$ corresponding to $\varepsilon_1^{\parallel}$ plots from Fig. 3.20 to Fig. 3.36a.

E_z (V/Å)	P1 (eV)	A1	P2 (eV)	A2	P3 (eV)	A3	P4 (eV)	A4
0.0	-	-	10.19	3.02	14.12	1.44	16.50	0.82
0.1	-	-	10.15	2.96	13.85	1.51	15.95	0.75
0.2	-	-	10.08	2.85	13.19	1.48	-	-
0.3	-	-	9.95	2.68	14.12	1.39	-	-
0.4	1.48	1.37	9.98	2.66	14.13	1.37	-	-
0.5	1.79	1.39	10.02	2.66	14.13	1.37	-	-
0.6	1.92	1.42	10.03	2.63	14.13	1.37	-	-
0.7	1.92	1.44	10.03	2.59	12.06	1.43	-	-
0.8	2.07	1.44	10.04	2.58	12.15	1.53	-	-
0.9	2.17	1.45	10.06	2.57	12.20	1.58	-	-
1.0	2.24	1.48	10.07	2.55	12.32	1.64	-	-
1.2	2.31	1.52	10.08	2.51	12.44	1.76	-	-
1.5	2.36	1.60	10.08	2.47	12.48	1.88	-	-
1.7	2.46	1.62	10.07	2.43	12.49	1.82	-	-
2.0	2.75	1.60	10.08	2.42	12.51	1.66	-	-
2.2	2.82	1.62	10.08	2.40	13.60	1.66	-	-
2.5	2.89	1.66	10.07	2.37	13.66	1.72	-	-

Table 3.5: Position of peaks and their amplitudes between 0 eV and 16.50 eV for the E-field magnitudes $0.0 \text{ V/Å} \leq E_z \leq 2.5 \text{ V/Å}$ corresponding to $\epsilon_1^\perp$ plots from Fig. 3.20 to Fig. 3.36b.

In Table 3.7 when the magnitude of applied external static electric field is 0.3 V/Å , P4 is at 10.19 eV, P5 is at 12.12 eV, P6 is at 14.45 eV such that P4 and P6 correspond to $\pi \rightarrow \sigma^*$ and $\sigma \rightarrow \pi^*$ transitions, respectively. Additionally, the transition that takes place related to P5 is $\sigma \rightarrow \sigma^*$ transition which is from around -6.6 eV towards near +5.5 eV by its DOS plot and related electronic band diagram. Above, $\pi \rightarrow \sigma^*$ transition takes place due to P4 and $\sigma \rightarrow \pi^*$ transition occurs due to P6 as explained in detail.

E_z (V/Å)	P1 (eV)	A1	P2 (eV)	A2	P3 (eV)	A3	P4 (eV)	A4	P5 (eV)	A5	P6 (eV)	A6
0.0	1.32	4.90	1.95	2.00	2.81	2.26	3.76	3.08	14.13	1.69	15.26	1.24
0.1	1.32	4.89	1.95	2.00	2.81	2.26	3.76	3.08	14.12	1.74	15.26	1.29
0.2	1.32	4.89	1.95	2.00	2.81	2.26	3.76	3.07	14.05	1.70	15.26	1.34
0.3	1.32	4.89	1.95	2.00	2.81	2.26	3.76	3.07	14.36	1.65	15.24	1.32
0.4	1.32	4.88	1.95	2.00	2.81	2.26	3.76	3.07	14.36	1.64	15.25	1.32
0.5	1.32	4.76	1.95	1.99	2.81	2.26	3.76	3.07	14.05	1.69	15.25	1.35
0.6	1.32	4.48	1.95	1.98	2.81	2.25	3.77	3.07	14.06	1.73	15.26	1.35
0.7	1.32	4.15	1.95	1.97	2.81	2.25	3.77	3.07	14.07	1.75	15.26	1.34
0.8	1.32	3.79	1.95	1.96	2.81	2.25	3.77	3.07	14.10	1.79	15.26	1.31
0.9	1.32	3.43	1.95	1.94	2.81	2.24	3.76	3.06	14.11	1.81	15.27	1.30
1.0	1.32	3.07	1.95	1.92	2.81	2.24	3.76	3.06	14.12	1.83	15.27	1.29
1.2	1.32	2.41	1.95	1.86	2.81	2.23	3.76	3.06	14.14	1.82	15.27	1.29
1.5	1.32	1.51	1.95	1.72	2.82	2.22	3.76	3.05	14.16	1.73	15.28	1.29
1.7	1.32	0.99	1.95	1.57	2.82	2.21	3.76	3.05	14.16	1.74	15.28	1.28
2.0	1.32	0.45	1.95	1.26	2.82	2.19	3.76	3.05	14.16	1.77	15.28	1.26
2.2	1.32	0.25	1.95	1.02	2.82	2.17	3.77	3.04	14.17	1.80	15.29	1.26
2.5	1.32	0.11	1.95	0.71	2.82	2.12	3.77	3.04	14.18	1.75	15.29	1.27

Table 3.6: Position of peaks and their amplitudes between 0 eV and 16 eV for the E-field magnitudes $0.0 \text{ V/Å} \leq E_z \leq 2.5 \text{ V/Å}$ corresponding to $\varepsilon_2^{\parallel}$ plots from Fig. 3.20 to Fig. 3.36c.

E_z (V/Å)	P1 (eV)	A1	P2 (eV)	A2	P3 (eV)	A3	P4 (eV)	A4	P5 (eV)	A5	P6 (eV)	A6
0.0	-	-	-	-	-	-	10.38	1.88	-	-	14.45	2.01
0.1	-	-	-	-	-	-	10.35	1.81	-	-	14.45	1.95
0.2	-	-	-	-	-	-	10.29	1.66	-	-	14.45	1.86
0.3	-	-	-	-	-	-	10.19	1.37	12.12	0.70	14.45	1.87
0.4	1.58	0.10	-	-	-	-	10.29	1.33	12.62	0.78	14.16	1.87
0.5	1.89	0.13	-	-	-	-	10.25	1.35	12.63	0.79	14.46	1.85
0.6	2.02	0.17	3.29	0.037	-	-	10.27	1.31	12.52	0.85	14.47	1.86
0.7	2.02	0.23	3.32	0.044	-	-	10.34	1.26	12.53	0.95	14.48	1.86
0.8	2.17	0.22	3.51	0.056	4.38	0.031	10.29	1.25	12.37	1.01	14.48	1.85
0.9	2.27	0.24	3.64	0.062	4.52	0.039	10.31	1.25	12.43	1.07	14.48	1.85
1.0	2.34	0.29	3.70	0.068	4.62	0.040	10.32	1.23	12.50	1.14	14.48	1.85
1.2	2.41	0.38	3.78	0.079	4.76	0.042	10.34	1.19	12.56	1.18	14.49	1.88
1.5	2.46	0.52	3.89	0.086	4.92	0.044	10.37	1.13	13.31	1.18	14.51	1.88
1.7	2.56	0.56	3.99	0.092	4.99	0.051	10.38	1.08	13.33	1.27	14.52	1.89
2.0	2.85	0.51	4.25	0.13	5.25	0.078	10.35	1.08	12.96	0.97	14.54	1.98
2.2	2.92	0.55	4.35	0.13	5.36	0.085	10.34	1.06	12.98	0.92	14.55	2.05
2.5	2.99	0.64	4.47	0.14	5.51	0.088	10.31	1.04	12.99	0.85	14.56	2.22

Table 3.7: Position of peaks and their amplitudes between 0 eV and 16 eV for the E-field magnitudes $0.0 \text{ V/Å} \leq E_z \leq 2.5 \text{ V/Å}$ corresponding to $\varepsilon_2^\perp$ plots from Fig. 3.20 to Fig. 3.36d.

In Table 3.7 for $E_z = 0.4 \text{ V/\AA}$, one peak appeared at 1.58 eV with an amplitude of 0.10 (Fig. 3.24d) that is indicating that for 0.4 V/ $\text{\AA}$ electric field amplitude, a transition occurred with an energy difference of 1.58 eV. To deduce which transition this is, I refer back to Fig. 3.5, i.e., the electronic band structure and DOS plot for $E_z = 0.4 \text{ V/\AA}$. A possible $\sigma^* \rightarrow \pi^*$ transition is observed from 0.21 eV towards 1.79 eV. Transition due to the peak at 10.29 is $\pi \rightarrow \sigma^*$ starting from around -6.5 eV in the corresponding DOS plot and reaches around 3.8 eV there. This transition is expected since that peak in Fig. 3.24d is due to $\pi \rightarrow \sigma^*$ transition as drawn in Fig. 3.20d and the peak observed at 10.29 eV is its slightly shifted version. The peak at 12.62 eV corresponding to P5 is due to $\sigma \rightarrow \sigma^*$ transition. Moreover, the peak at 14.16 eV (P6) corresponds to $\sigma \rightarrow \pi^*$ transition which is from -12.09 eV to 2.08 eV as can be seen in DOS and electronic band structure plots. Throughout data tabulated in Table 3.7, shifts corresponding to P4 and P6 are related to $\pi \rightarrow \sigma^*$ and $\sigma \rightarrow \pi^*$ transitions, respectively, which are verified from corresponding DOS plots and electronic band structures. As identified above, P5 is corresponding to $\sigma \rightarrow \pi^*$ transition for $E_z = 0.4$. After checking DOS & electronic band diagrams for all E_z values from Fig. 3.6 to Fig. 3.17, it is verified that P5 is referring to $\sigma \rightarrow \pi^*$ transition. However, I analyze all of the peaks in Table 3.7 in detail as can be seen from the following explanations.

From Table 3.7 and Fig. 3.25d, at 1.89 eV a new peak is observed when $E_z = 0.5 \text{ V/\AA}$. After comparison with corresponding DOS & band structure data, this transition is due to $\sigma^* \rightarrow \pi^*$ transition from 0.00 eV to 1.89 eV. $\sigma \rightarrow \pi^*$ transition took place from -12.16 eV to 2.30 eV whereas the transition corresponding to $\pi \rightarrow \sigma^*$ is observed from -7.31 eV to 2.98 eV. Moreover, P5, that is at 12.63 eV is a $\sigma \rightarrow \sigma^*$ transition from -6.5 eV to 6.2 eV.

When E-field amplitude is $0.6 \text{ V/\AA}$, $\pi \rightarrow \sigma^*$ transition takes place between approximately -7.26 eV and 3.01 eV, $\sigma \rightarrow \pi^*$ transition occurs from around -12.45 eV towards near 1.99 eV. The peak at 2.02 eV, P1, in Fig. 3.26d corresponds

to $\sigma^* \rightarrow \pi^*$ transition between -0.03 eV to 1.9 eV whereas P5 is present due to the transition that is occurring from -12.47 eV to 0.05 eV which is a $\sigma \rightarrow \sigma^*$ transition. Starting from this value of E_z , a new peak appeared denoted by P2 at 3.29 eV that may be a transition from -1.85 eV to 1.45 eV that is indicating a $\pi \rightarrow \pi^*$ transition.

For $E_z = 0.7 \text{ V/\AA}$, transition corresponding to P4 takes place between near from -7.20 eV to 3.18 eV, transition related to P6 occurs from -10.1 eV to 4.3 eV and those two transitions are $\pi \rightarrow \sigma^*$ and $\sigma \rightarrow \pi^*$ transitions, respectively. At 3.32, P2 appeared that is indicating a $\pi \rightarrow \pi^*$ transition between -1.77 eV to 1.53 eV. P1 is due to $\sigma^* \rightarrow \pi^*$ transition from -0.061 eV to 1.96 eV whereas P5 is corresponding to $\sigma \rightarrow \sigma^*$ transition from -6.2 eV towards 6.3 eV.

When the amplitude of the E-field is $0.8 \text{ V/\AA}$, at 10.29 eV P4 is referring to $\pi \rightarrow \sigma^*$ transition takes place from -6.07 eV to 4.22 eV, at 14.48 eV corresponding to P6 $\sigma \rightarrow \pi^*$ transition occurs from -13.87 eV to 0.61 eV, the transition representing P5 at 12.37 eV is a $\sigma \rightarrow \sigma^*$ transition from -6.07 eV to 6.3 eV, $\sigma^* \rightarrow \pi^*$ transition that is representing P1 is from -0.063 eV to 2.11 eV, and $\pi \rightarrow \pi^*$ transition that is representing P2 takes place from -1.74 eV to 1.77 eV. In addition to those transitions, new peak which I called P3 appeared starting from this electric field amplitude which is observed at 4.38 eV and is corresponding to a $\sigma \rightarrow \pi^*$ transition approximately from -2.88 eV to 1.48 eV. The rest of tabulated data in Table 3.7 contain all of the peaks.

For $E_z = 0.9 \text{ V/\AA}$, P1 is at 2.27 eV that represents $\sigma^* \rightarrow \pi^*$ transition from -0.10 eV to 2.17 eV, P2 corresponds to $\pi \rightarrow \pi^*$ transition between -1.70 and 1.95 eV, $\sigma \rightarrow \pi^*$ transitions corresponding to P3 and P6 take place from near -2.8 eV to 1.7 eV, and from -12.51 eV towards 1.97 eV, respectively. $\pi \rightarrow \sigma^*$ transition occurs from -7.02 eV towards 3.29 eV. Eventually, P5 refers to a $\sigma \rightarrow \sigma^*$ transition between -6.00 eV to 6.43 eV.

In the case of $E_z = 1.0 \text{ V/\AA}$, P1 governs $\sigma^* \rightarrow \pi^*$ transition from - 0.083 eV to 2.26 eV, P2 at 3.70 eV is due to $\pi \rightarrow \pi^*$ transition from -1.71 eV to 1.99 eV, $\sigma \rightarrow \pi^*$ transitions related to P3 and P6 are from -2.77 eV towards 1.85 eV, and from -12.48 to 2.00 eV, respectively. P4 represents $\pi \rightarrow \sigma^*$ transition that takes place between -6.89 eV and 3.43 eV. $\sigma \rightarrow \sigma^*$ transition occurs from -6.03 eV towards 6.47 eV.

When $E_z = 1.2 \text{ V/\AA}$, $\sigma^* \rightarrow \pi^*$ transition is observed from -0.15 eV to 2.26 eV, $\pi \rightarrow \pi^*$ transition took place from -1.64 eV towards 2.14 eV, $\pi \rightarrow \sigma^*$ transition occurred between -6.85 eV and 3.49 eV, $\sigma \rightarrow \sigma^*$ transition took place from -5.95 eV to 6.61 eV. $\sigma \rightarrow \pi^*$ transitions related to P3 and P6 are from -2.69 eV to 2.07 eV, and -5.95 eV to 8.54 eV.

For $E_z = 1.5 \text{ V/\AA}$, $\sigma^* \rightarrow \pi^*$ transition corresponding P1 at 2.46 eV takes place from -0.18 eV to 2.28 eV whereas $\pi \rightarrow \pi^*$ transition is from around -1.55 eV towards 2.33 eV. For P3 and P6, $\sigma \rightarrow \pi^*$ transitions are observed from -2.65 eV to 2.27 eV, and from -5.85 eV towards 8.66 eV, respectively. $\pi \rightarrow \sigma^*$ transition takes place between -6.72 eV and 3.65 eV. Eventually, for this E-field amplitude, $\sigma \rightarrow \sigma^*$ transition takes place from -5.85 eV to 7.46 eV close to the M point in the fBZ.

In the case of $E_z = 1.7 \text{ V/\AA}$, $\sigma^* \rightarrow \pi^*$ transition takes place between -0.22 eV and 2.34 eV, $\pi \rightarrow \pi^*$ transition is observed to occur from -1.47 eV towards 2.52 eV, $\pi \rightarrow \sigma^*$ transition takes place from -6.65 eV to 3.73 that is observed at Γ point in the fBZ. $\sigma \rightarrow \sigma^*$ transition corresponding to P5 is observed from near -5.77 eV towards 7.56 eV near the M point in the fBZ. Eventually, $\sigma \rightarrow \pi^*$ transitions correspond to P3 and P6 take place from -2.53 eV to 2.46 eV, and from -5.77 eV towards 8.75 eV, respectively.

When $E_z = 2.0 \text{ V/\AA}$, for P3 and P6 $\sigma \rightarrow \pi^*$ transitions are observed from -2.43 eV to 2.85 eV, and from -12.71 eV to 1.83 eV. $\sigma^* \rightarrow \pi^*$ transition takes place between -0.26 eV and 2.59 eV, $\pi \rightarrow \pi^*$ transition is observed to occur from -1.40

eV to 2.85 eV, $\pi \rightarrow \sigma^*$ transition is between -6.61 eV and 3.74 eV, and $\sigma \rightarrow \sigma^*$ transition due to P5 takes place from -5.71 eV towards 7.25 eV between Γ and M points in the fBZ.

For $E_z = 2.2$ V/Å, $\sigma^* \rightarrow \pi^*$ transition that corresponds to P1 takes place from -0.30 eV to 2.62 eV, $\pi \rightarrow \pi^*$ transition is from 1.35 eV towards near 3.00 eV, $\pi \rightarrow \sigma^*$ transition that is corresponding to P4 is observed to occur from -6.13 eV to 4.21 eV between Γ and M points in the fBZ. Similar to $\pi \rightarrow \sigma^*$ transition, $\sigma \rightarrow \sigma^*$ transition that corresponds to P5 takes place between M and Γ points in the fBZ from -4.64 eV to 8.34 eV. For P3 $\sigma \rightarrow \pi^*$ transition is observed from -2.40 eV towards 2.96 eV, and the same transition for P6 is from -13.39 eV to 1.16 eV which occurs between M and Γ points in the fBZ that is starting from a point near K point and reaches π^* by getting closer to the Dirac point.

Eventually, for the last magnitude of applied external static electric field that is perpendicular to the single-layer graphene sheet, I finalize the analysis for transitions due to Table 3.7. In the case of $E_z = 2.5$ V/Å, $\sigma^* \rightarrow \pi^*$ transition that represents P1 is from -0.33 eV to 2.66 eV which takes place from Γ point towards around Dirac point in the fBZ. $\pi \rightarrow \pi^*$ transition that corresponds to P2 at 4.47 eV takes place from -1.27 eV to 3.20 eV between Γ and M points. $\pi \rightarrow \sigma^*$ transition takes place from -6.46 eV to 3.85 eV around Γ point. $\sigma \rightarrow \sigma^*$ transition that represents P5 takes place between Γ and M points (closer to M point) from -5.62 eV to 7.37 eV. Lastly, for P3 and P6 $\sigma \rightarrow \pi^*$ transitions occur from -2.41 eV to 3.10 eV, and from -13.33 eV towards 1.23 eV between either Γ and M points or between K and Γ points in the fBZ.

To summarize, electronic transitions represented in Table 3.7 are gathered in Table 3.8 in a nutshell. As mentioned several times previously, throughout this chapter possible interband transitions corresponding to the monolayer graphene are identified as $\pi \rightarrow \pi^*$ and $\sigma \rightarrow \sigma^*$ as shown in Fig. 3.20c. In addition to them, by Fig. 3.20d, other interband transitions are $\sigma \rightarrow \pi^*$ and $\pi \rightarrow \sigma^*$. Effect of external static electric field that is applied perpendicular to the monolayer graphene sheet showed itself in four of above cited transitions as described. In addition to those four transitions known well and showed in several works such as [49] and

[50], another electronic transition took place, that is, $\sigma^* \rightarrow \pi^*$ transition which is from the band corresponding to antibonding sp^2 orbitals, σ^* band, towards the band representing the antibonding p_z orbitals, that is, π^* band. $\sigma^* \rightarrow \pi^*$ transition is observed to take place from around Γ point towards around K point in the fBZ. As the value of E_z increased, σ^* band started to move below the level representing Fermi energy, E_F , which is set to zero for all band structure and DOS plots, and is identified as red dotted lines. By the movement of σ^* band from CB to VB -below E_F - starting by $E_z=0.5$ V/Å, there revealed more available states for electrons to fill in which is doping monolayer graphene by applying such an E-field. As can be seen from Fig. 3.6, the new structure in DOS plot near Fermi level is transpired due to the shift of σ^* band below E_F and it is now at -0.015 eV. Since monolayer graphene gets richer in electrons, identified as negative charge carriers, this doping is called n-doping. Hence, as the amplitude of perpendicularly applied external static electric field increased, single-layer graphene became n-doped due to $\sigma^* \rightarrow \pi^*$ interband transition. Another consequence of this introduced E-field is that, it enabled us to observe $\pi \rightarrow \pi^*$ and $\sigma \rightarrow \sigma^*$ transitions by using only $\varepsilon_2^\perp$ plots. In the previous works of scientists, $\pi \rightarrow \pi^*$ and $\sigma \rightarrow \sigma^*$ transitions could be determined from $\varepsilon_2^\parallel$ plot corresponding to the monolayer graphene. However, all transitions cited in Table 3.8 are obtained only from $\varepsilon_2^\perp$ data.

Transition	Related Peak
$\sigma^* \rightarrow \pi^*$	P1
$\pi \rightarrow \pi^*$	P2
$\sigma \rightarrow \pi^*$	P3 & P6
$\pi \rightarrow \sigma^*$	P4
$\sigma \rightarrow \sigma^*$	P5

Table 3.8: Transitions of electrons under E-field and the peaks corresponding to them by Table 3.7

By using Table 3.7, change of P1, P3, and P4 (corresponding to $\sigma^* \rightarrow \pi^*$, $\sigma \rightarrow \pi^*$, and $\pi \rightarrow \sigma^*$ transitions, respectively) due to E-field amplitude is illustrated in Fig. 3.37, 3.38, and 3.39, respectively.

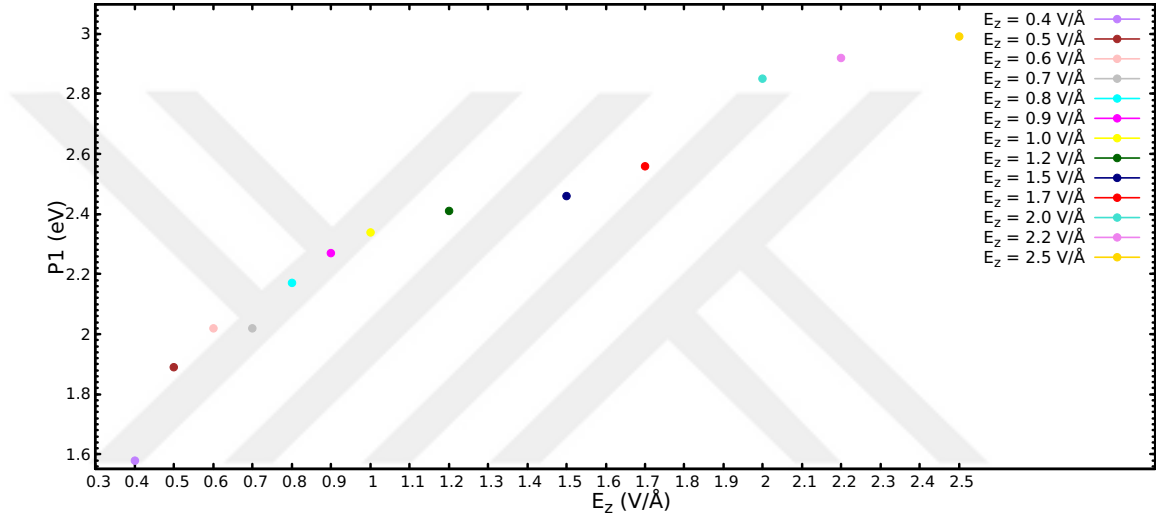


Figure 3.37: Peak amplitude versus E_z plot corresponding to $\sigma^* \rightarrow \pi^*$ transition by Table 3.7.

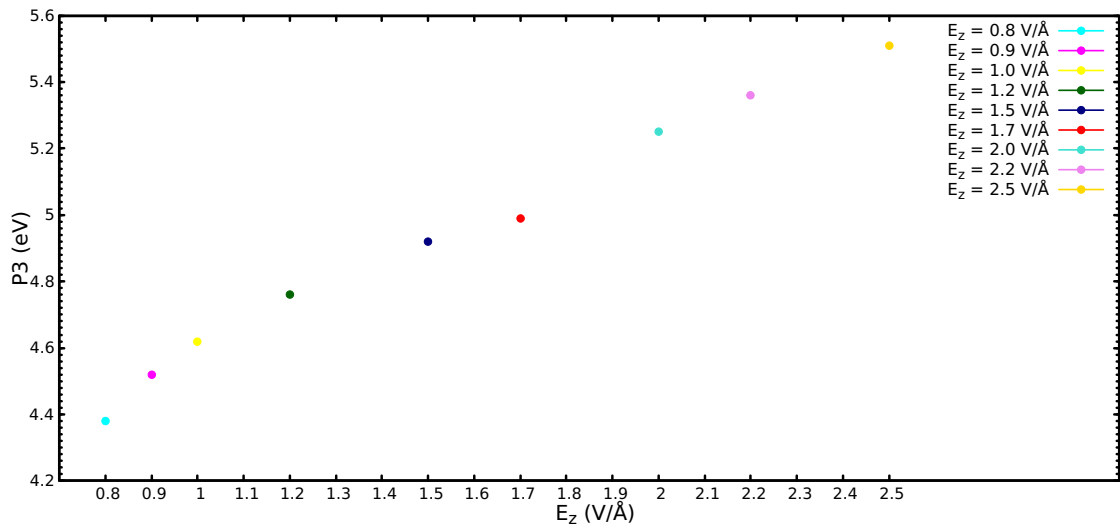


Figure 3.38: Peak amplitude versus E_z plot corresponding to $\sigma \rightarrow \pi^*$ transition by Table 3.7.

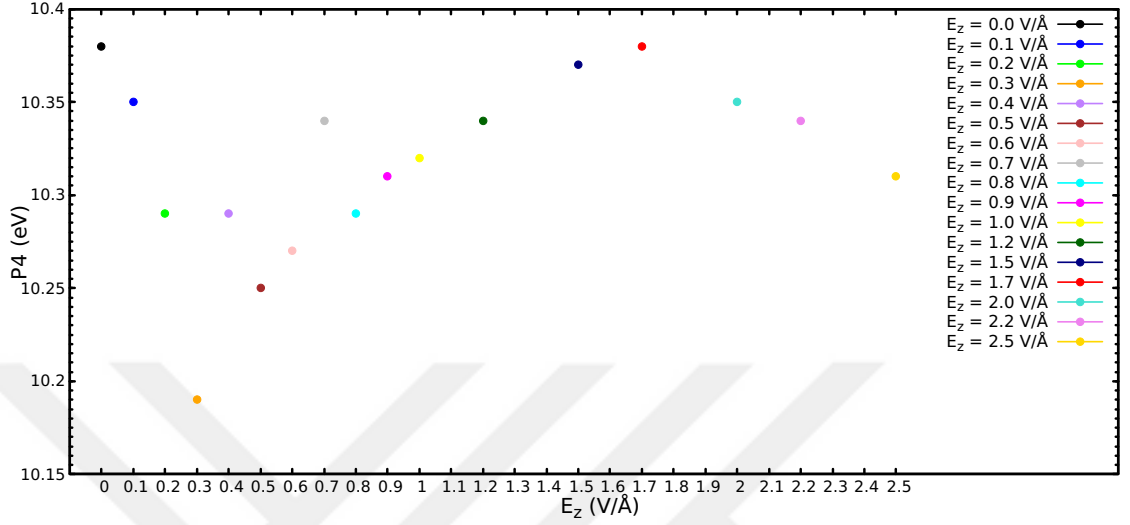


Figure 3.39: Peak amplitude versus E_z plot corresponding to $\pi \rightarrow \sigma^*$ transition by Table 3.7.

As shown in Fig. 3.37, P1 started to appear when $E_z \geq 0.4$ V/Å. For 0.6 V/Å $\leq E_z \leq 0.7$ V/Å, peaks remained in the same position, but except this, peaks corresponding to $\sigma^* \rightarrow \pi^*$ blueshifted as the strength of E-field is increased. For the peak representing $\sigma \rightarrow \pi^*$ transition, it is first observed when $E_z=0.8$ V/Å and P3 also blueshifted by increasing magnitudes of E-field. However, in Fig. 3.39, corresponding to $\pi \rightarrow \sigma^*$ transition, there is neither gradually increase nor piecemeal decrease. There is a gradual decrease for 0.0 V/Å $\leq E_z \leq 0.3$ V/Å which might be related to the linear increase observed in the same interval for the Fermi energy in Fig. 3.18b. For 0.8 V/Å $\leq E_z \leq 1.7$ V/Å peaks blueshifted. However for $E_z \geq 1.7$ V/Å, peaks redshifted.

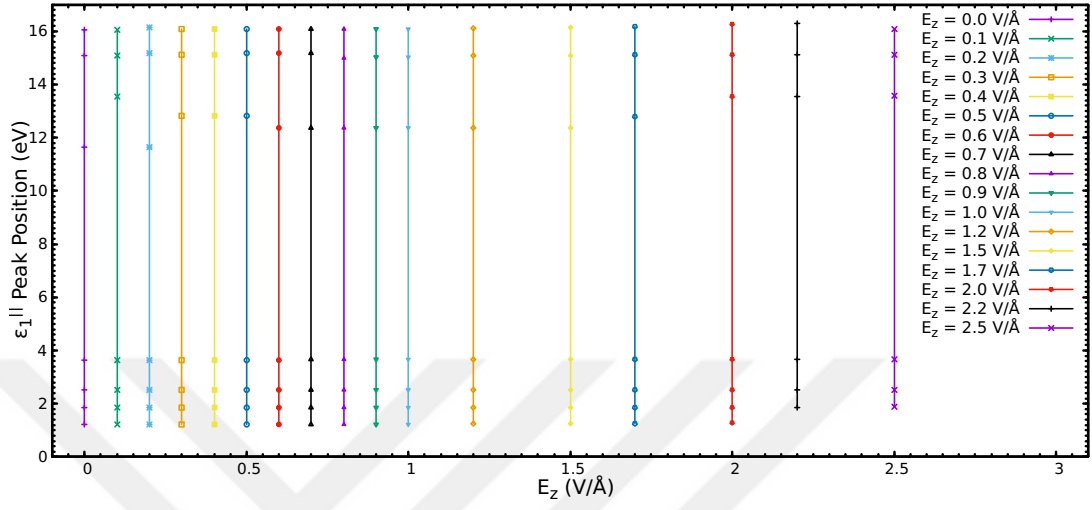
Since $\pi \rightarrow \pi^*$ and $\sigma \rightarrow \sigma^*$ transitions can be detected by $\varepsilon_2^{\parallel}$ plots as identified at the beginning of Chapter 3.2, it may make sense to investigate those transitions from the table corresponding to the peak data of $\varepsilon_2^{\parallel}$, i.e., Table 3.6. However, it was also possible to detect those two above-mentioned transitions from Table 3.7 in which data were tabulated from $\varepsilon_2^{\perp}$. They were mentioned in detail throughout Chapter 3.2. In Table 3.6, P4 corresponds to $\pi \rightarrow \pi^*$ transition whereas P5 represents $\sigma \rightarrow \sigma^*$ transition which may be seen without difficulty from corresponding $\varepsilon_2^{\parallel}$ figures for all values of the external static electric field. In

the P4 column, peaks are either at 3.76 eV or 3.77 eV which might be regarded as for all values of E_z , the position of the fourth peak remained the same which means there is neither blueshift nor redshift. Moreover, the same statement can be concluded for amplitudes corresponding to P4 as well. Peak positions corresponding to $\sigma \rightarrow \sigma^*$ transition vary between 14.05 and 14.36 eV. This difference is not large as well. The same can be applied to amplitudes of mentioned peaks.

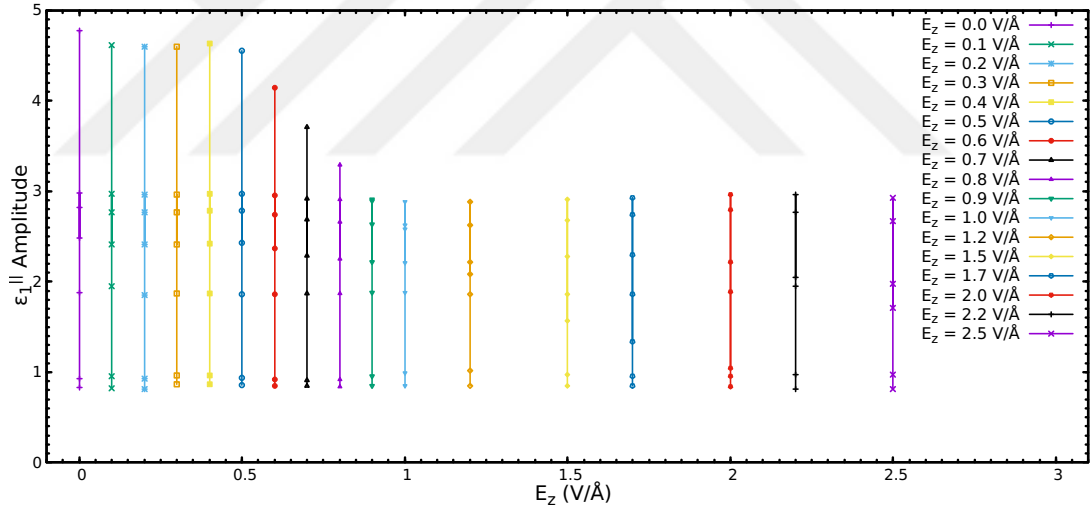
For the high energy zone of $\varepsilon_2^\perp$ plots, i.e., after 15 eV, with the external electric field, for $0.1 \text{ V/\AA} \leq E_z \leq 0.2 \text{ V/\AA}$ peaks redshifted whereas between $0.3 \text{ V/\AA}$ and $2.5 \text{ V/\AA}$ electric field amplitudes, those peaks blueshifted. Eventually, for the middle region of $\varepsilon_2^\perp$ data corresponding to energies between 10 eV and 15 eV, after $0.4 \text{ V/\AA}$ new peaks appeared around 12.5 eV which became more apparent as the value of applied external electric field increased. Moreover, this new peaks blueshifted for $1.5 \text{ V/\AA} \leq E_z \leq 2.5 \text{ V/\AA}$. For $E_z = 2.2 \text{ V/\AA}$ and $E_z = 2.5 \text{ V/\AA}$, amplitude of the peaks corresponding to $\sigma \rightarrow \pi^*$ strengthened.

Before completing this chapter, from Fig. 3.40 to Fig. 3.43, position and amplitude of the peaks tabulated in Tables 3.4, 3.5, 3.6, 3.7 are plotted against E_z to compare changes in P and A visually as well.

Let me start with Fig. 3.40. In Table 3.4, except for P1 when $E_z = 2.2 \text{ V/\AA}$ and $E_z = 2.5 \text{ V/\AA}$, all seven peaks are present for all E-field magnitudes. There are no vital changes observed for P1, P2, P3, P4, P6 and P7. However some fluctuations are observed in P5 especially for $0.0 \text{ V/\AA} \leq E_z \leq 0.3 \text{ V/\AA}$ and for $1.5 \text{ V/\AA} \leq E_z \leq 2.0 \text{ V/\AA}$. In the last mentioned interval, peaks linearly blueshifted. A1 decreased drastically by increasing E_z . However, no vital changes are observed for A2, A3, A4, A5, A6 and A7.

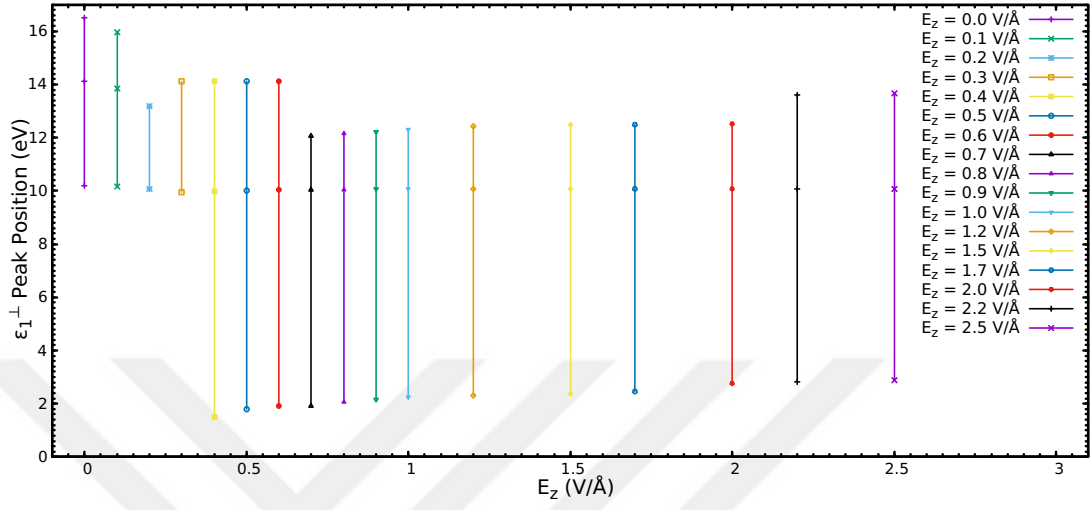


(a)

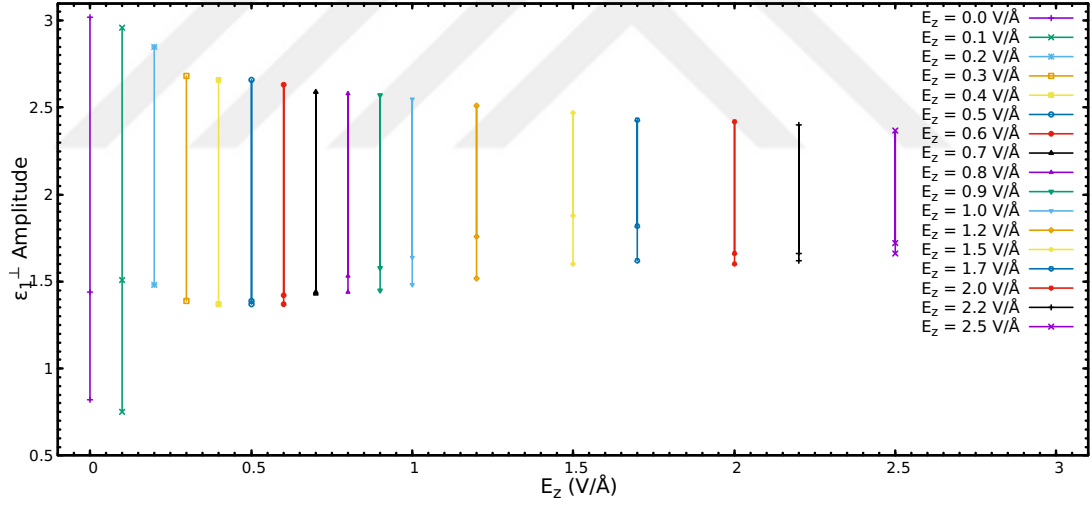


(b)

Figure 3.40: Position of the peaks and corresponding amplitudes under the influence of E-field. (a) Peak position versus E-field plot for $\varepsilon_1^{\parallel}$. (b) Amplitude versus E-field plot for $\varepsilon_1^{\parallel}$.

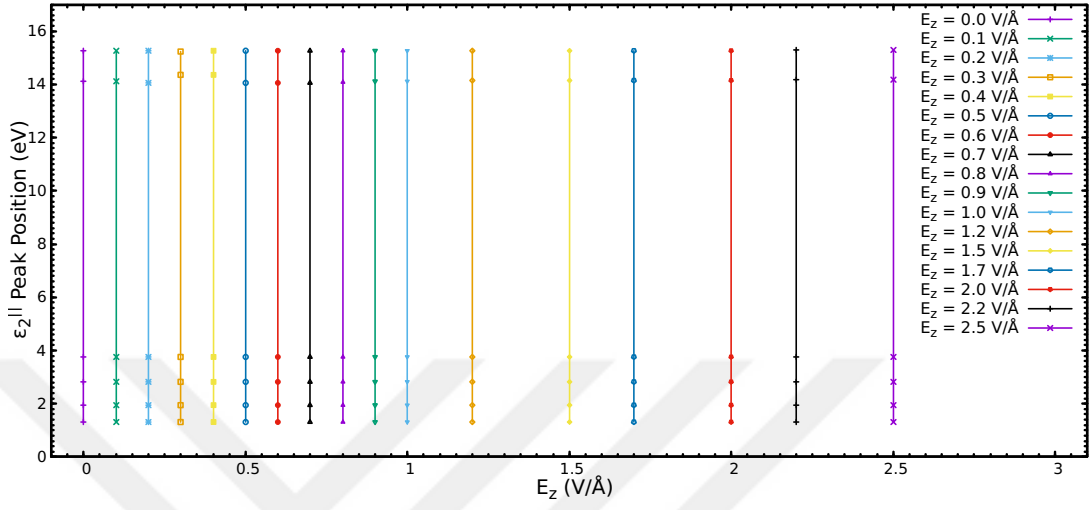


(a)

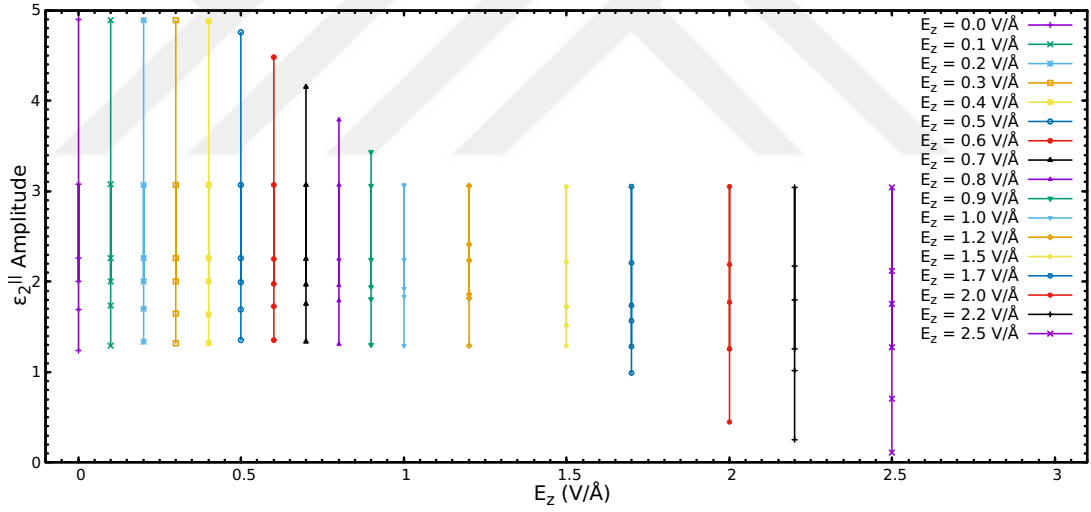


(b)

Figure 3.41: Position of the peaks and corresponding amplitudes under the influence of E-field. (a) Peak position versus E-field plot for $\varepsilon_1^\perp$. (b) Amplitude versus E-field plot for $\varepsilon_1^\perp$.

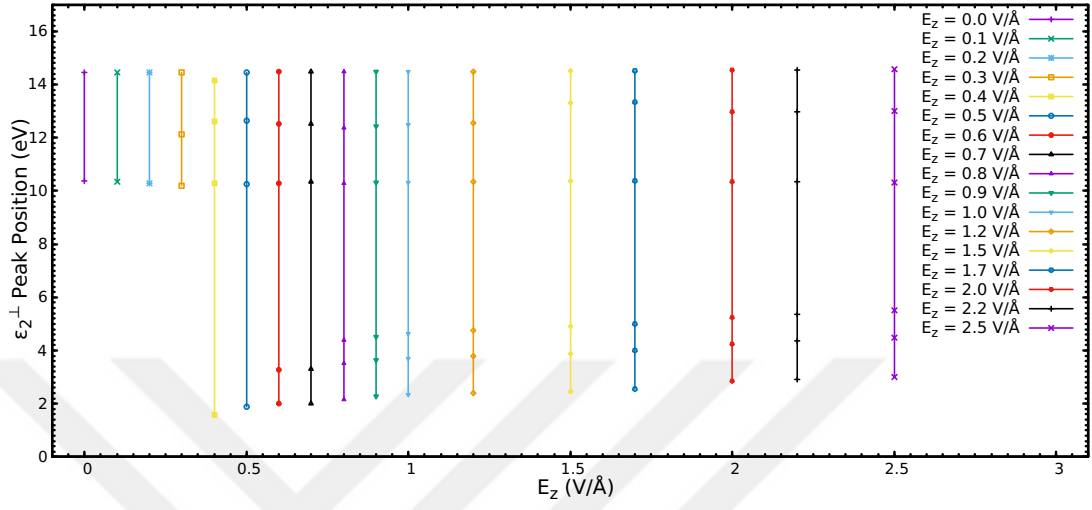


(a)

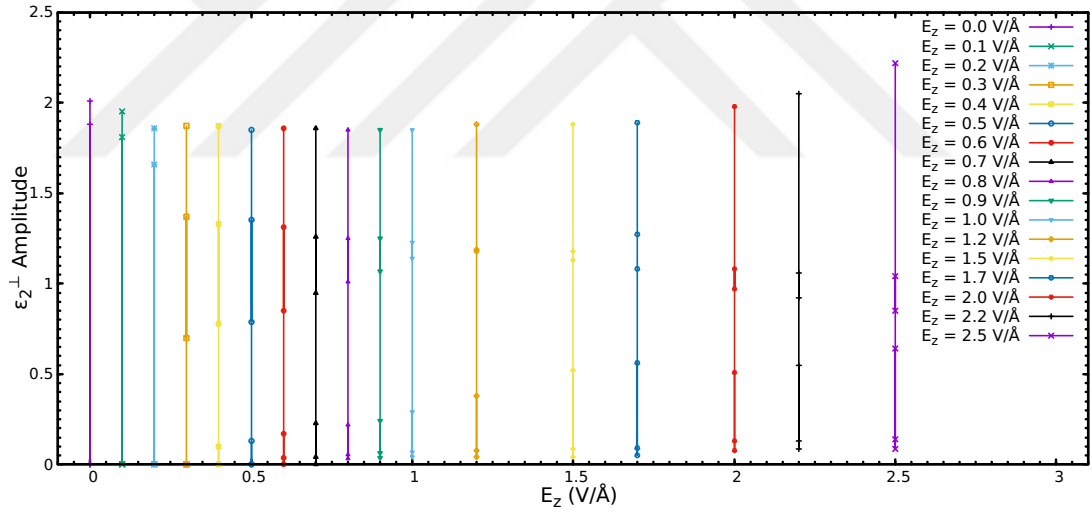


(b)

Figure 3.42: Position of the peaks and corresponding amplitudes under the influence of E-field. (a) Peak position versus E-field plot for $\varepsilon_2^{\parallel}$. (b) Amplitude versus E-field plot for $\varepsilon_2^{\parallel}$.



(a)



(b)

Figure 3.43: Position of the peaks under the influence of E-field. (a) Peak position versus E-field plot for $\epsilon_2^\parallel$. (b) Peak position versus E-field plot for $\epsilon_2^\perp$.

In Fig. 3.41, first peak is not present for $0.0 \text{ V/\AA} \leq E_z \leq 0.3 \text{ V/\AA}$, and last peak is not present for $0.2 \text{ V/\AA} \leq E_z \leq 2.5 \text{ V/\AA}$. As explained for Fig. 3.37, For $0.6 \text{ V/\AA} \leq E_z \leq 0.7 \text{ V/\AA}$, P1 remained in the same position. Except this, all P1 data shows that blueshift is observed as the strength of E-field is increased. For P3, some fluctuations are observed between $0.0 \text{ V/\AA} \leq E_z \leq 0.3 \text{ V/\AA}$ and from $0.6 \text{ V/\AA}$ to $0.7 \text{ V/\AA}$ there is a sharp decrease, but after $0.7 \text{ V/\AA}$, P3 blueshifted gradually. Except for $1.7 \text{ V/\AA} \leq E_z \leq 2.2 \text{ V/\AA}$ A1 increased gradually, whereas a gradual decrease is observed for A2. However, in some regions A3 increases and decreases, therefore it is fluctuating.

In Fig. 3.42, P1 and P2 remained at the exact position with the no-E-case whereas A1 and A2 decreased drastically even though for $0.0 \text{ V/\AA} \leq E_z \leq 0.4 \text{ V/\AA}$ both of the amplitudes almost did not change. P3, P4, and P5 did not remain at the same position for all amplitudes of E-field unlike P1 and P2 did. However, the change of peak positions corresponding to P3, P4, and P5 almost remained the same, in other words, one vital changes have observed. The same statement is applied also for their amplitudes A3, A4, and A5.

Finally, first three peaks are not present for $0.0 \text{ V/\AA} \leq E_z \leq 0.3 \text{ V/\AA}$ as can be seen by Table 3.7 and Fig. 3.43. P5 is absent for $0.0 \text{ V/\AA} \leq E_z \leq 0.2 \text{ V/\AA}$, and when E_z is $0.4 \text{ V/\AA}$ and $0.5 \text{ V/\AA}$ there are no P2 and P3 observed corresponding to them. Lastly, for $0.6 \text{ V/\AA} \leq E_z \leq 0.7 \text{ V/\AA}$ no P3 has been detected. Blueshift is observed gradually for P1, P2, and P3. A1, A2, and A3 increased by increasing strength of E-field, as well. However, P4 and P6 are almost did not change, therefore neither a considerable blueshift nor redshift has been observed related to last cited two peaks. A4 decreased by increasing E-field amplitudes. However A6 and A5 fluctuated so that A5 increased up to $E_z = 1.7 \text{ V/\AA}$, then started to decrease.

Chapter 4

Electronic and Optical Properties of Monolayer Molybdenum Carbide under the Influence of External Static Electric Field

In this chapter, the effects of the E-field applied perpendicularly on 2D molybdenum carbide, i.e., Mo_2C are investigated. Geometry optimizations, electronic band structure calculations, DOS and PDOS calculations, and optical properties involving ε_1 and ε_2 are investigated by the ground state calculations from first principles based on DFT. Calculations have been implemented by using QE [65, 66, 67]. Ground state SCF calculations have been implemented via pw.x whereas optical properties are obtained by epsilon.x code [72]. Optical calculations made possible to gather information corresponding to the interband transitions between electronic states in the absence and presence of E-field that is applied between 0.1 V/Å to 2.5 V/Å to the system and all results are compared with those in the absence of the external field.

4.1 Electronic Properties

The convergence threshold for the total energy is utilized as 1×10^{-8} Ry in the calculations. For the structural optimization, the convergence threshold for the forces is used as 1×10^{-3} Ry, whereas the convergence threshold for stress was 0.5 kbar. The distance between nearest-neighboring Mo atoms is obtained as 2.97 Å, the distance between nearest-neighboring C atoms is determined as 3.058 Å whereas for nearest-neighboring Mo and C atoms, it is found as 2.13 Å after structural optimization. To prevent interlayer interactions a vacuum of 24.6 Å is introduced to the primitive unit cell of 2D Mo_2C along the z-axis. Both C and Mo atoms are described by norm-conserving pseudo-potentials [74, 83]. Exchange-correlation functional is used as VDW-DF2 to include van der Waals interactions [70]. For geometry optimization and electronic band structure calculations, first Brillouin zone is sampled on a 9x9x1 Monkhorst-Pack k-mesh [73], whereas for DOS calculations k-mesh sampling was 39x39x1. The kinetic energy cutoff for the plane waves is determined as 90 Ry. To smoothen the occupied electronic states near the Fermi level, Gaussian smearing is utilized during performing SCF calculations. However, for DOS calculations tetrahedron technique is used to be more precise for the metallic system.

Between Figures 4.3 and 4.13 electronic band structure and DOS plots under the influence of E-field are displayed for this system between 0.1 V/Å and 2.5 V/Å.

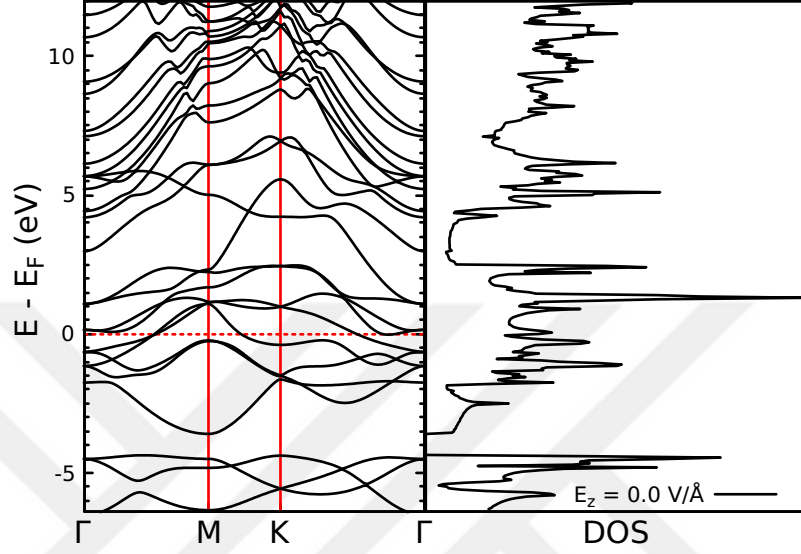


Figure 4.1: Electronic band diagram and DOS of 2D Mo_2C in the absence of E-field.

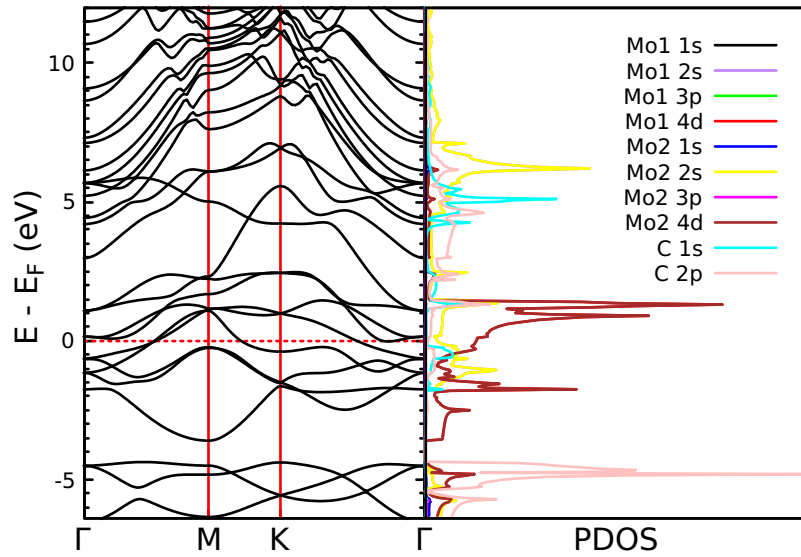


Figure 4.2: Electronic band diagram and projected density of states of 2D Mo_2C in the absence of external electric field.

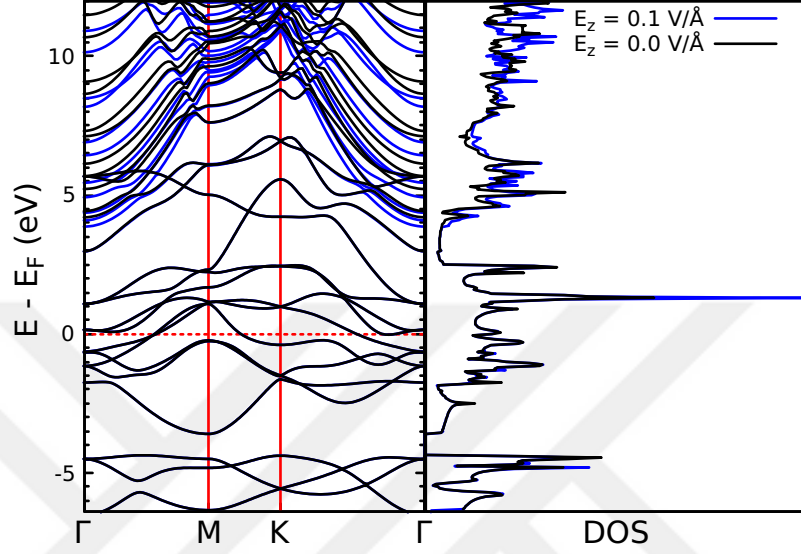


Figure 4.3: Electronic band diagram and DOS of 2D Mo_2C in the presence of an E-field of magnitude $E_z=0.1 \text{ V/\AA}$.

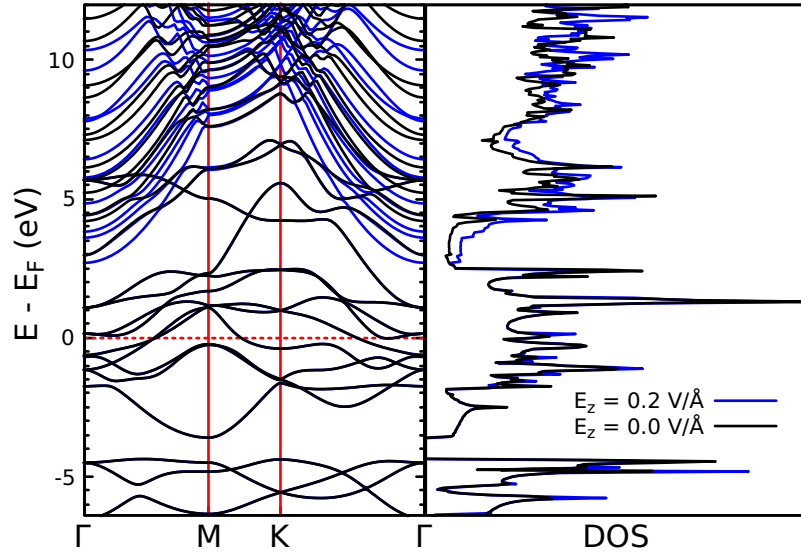


Figure 4.4: Electronic band diagram and DOS of 2D Mo_2C under the influence of an external electric field of magnitude $E_z=0.2 \text{ V/\AA}$.

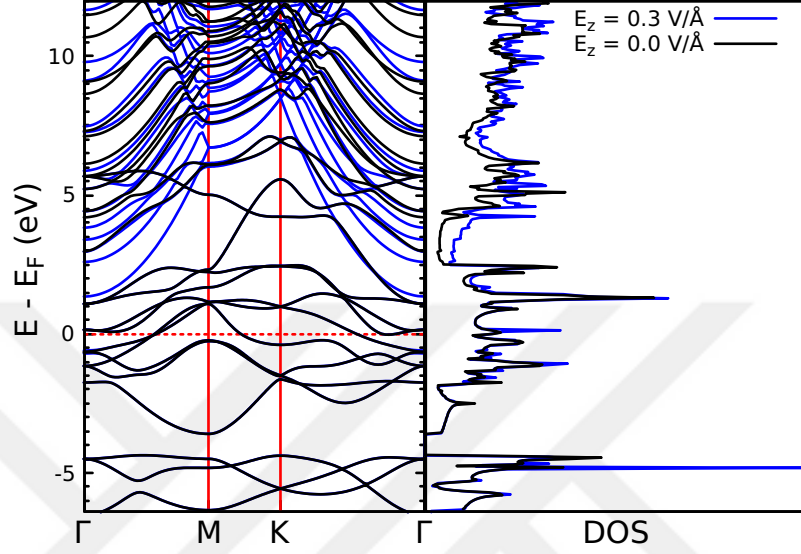


Figure 4.5: Electronic band diagram and DOS of 2D Mo_2C when the amplitude of the applied electric field is $E_z=0.3 \text{ V/\AA}$.

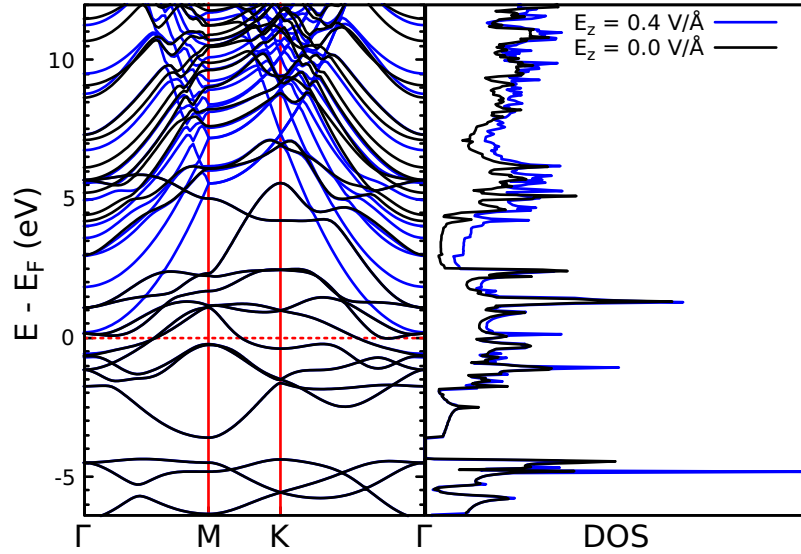


Figure 4.6: Electronic band diagram and DOS of 2D Mo_2C under $E_z=0.4 \text{ V/\AA}$.

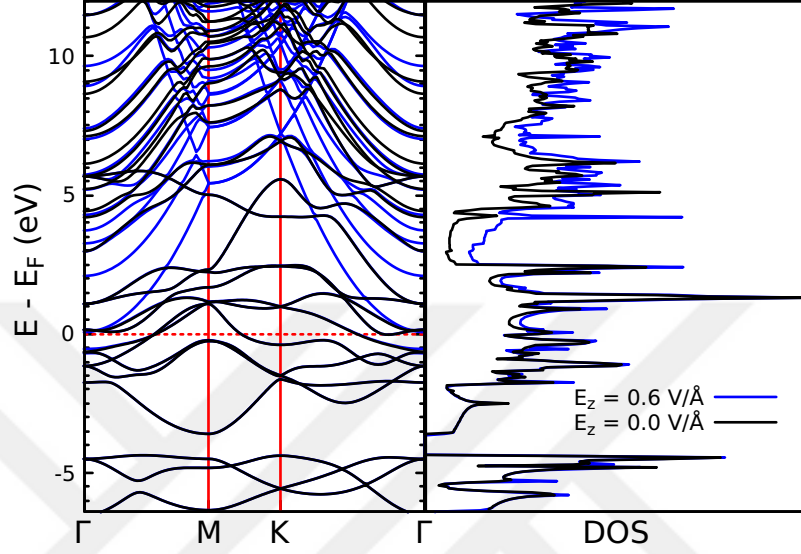


Figure 4.7: Electronic band diagram and DOS of 2D Mo_2C under the influence of an E-field strength of $E_z=0.6$ V/Å.

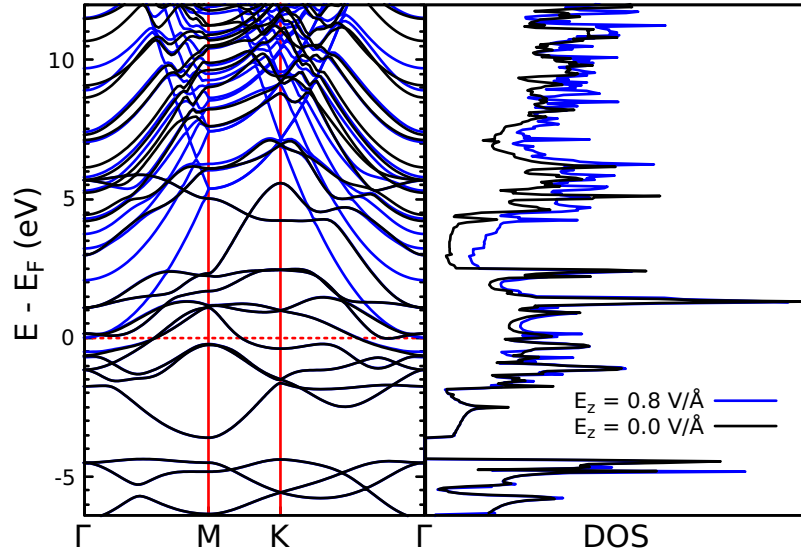


Figure 4.8: Electronic band diagram and DOS of 2D Mo_2C when the strength of the applied electric field is $E_z=0.8$ V/Å.

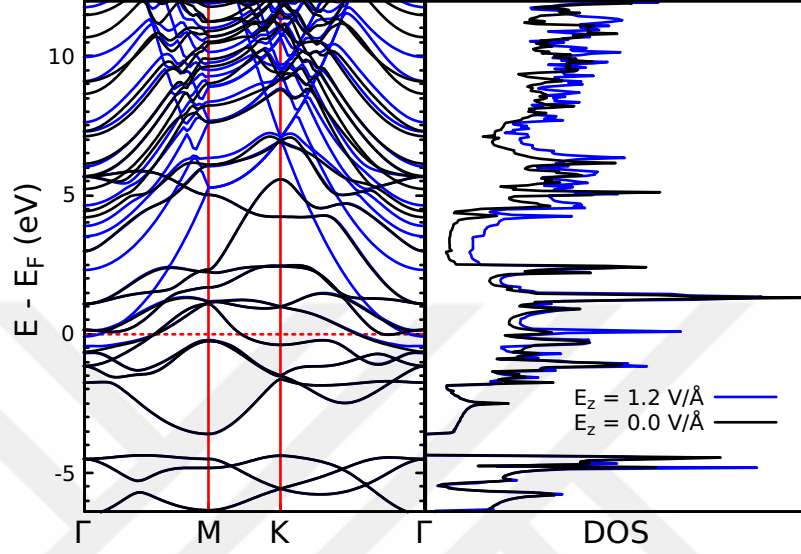


Figure 4.9: Electronic band diagram and DOS of 2D Mo_2C under the influence of an E-field strength of $E_z=1.2$ V/Å.

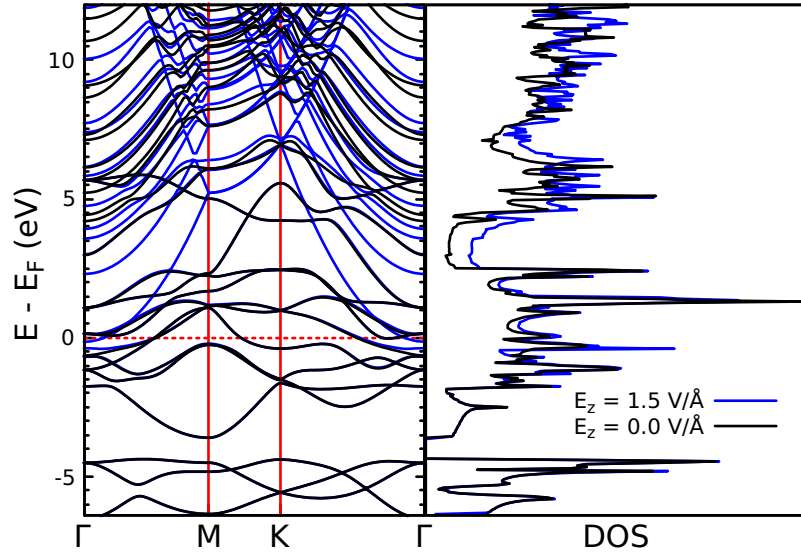


Figure 4.10: Electronic band diagram and DOS of 2D Mo_2C when the amplitude of the applied electric field is $E_z=1.5$ V/Å.

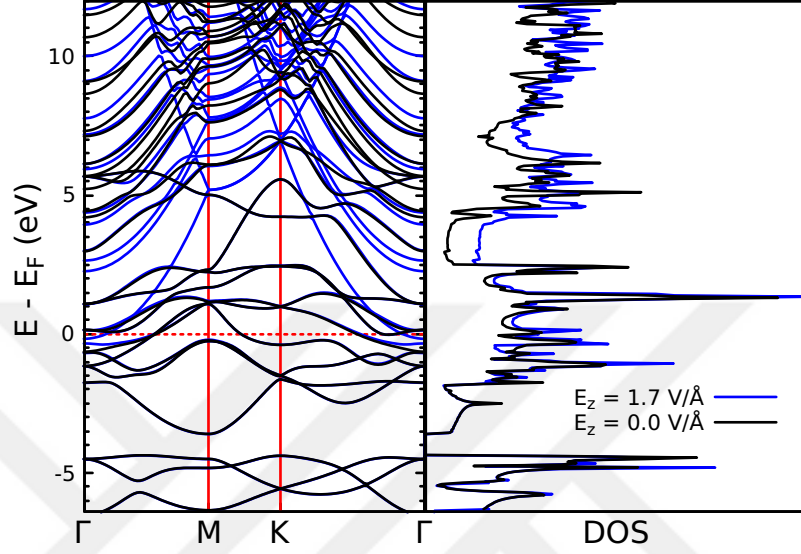


Figure 4.11: Electronic band diagram and DOS of 2D Mo_2C when the strength of the applied electric field is $E_z = 1.7 \text{ V/\AA}$.

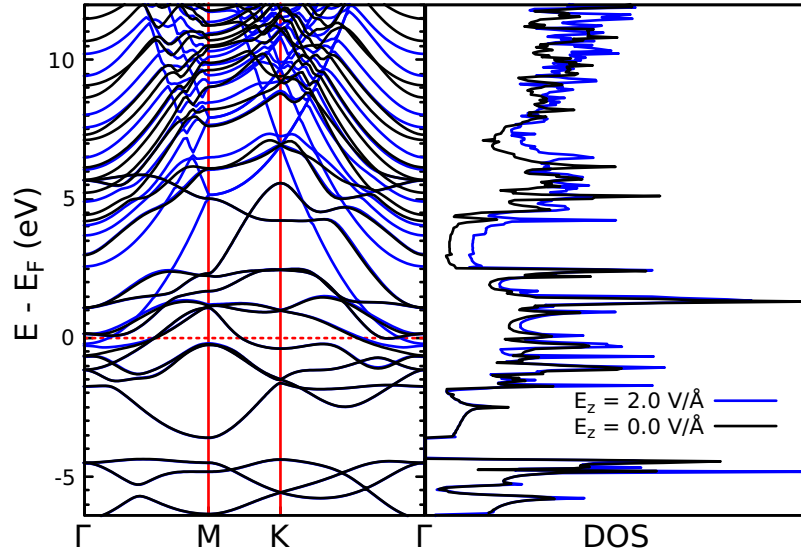


Figure 4.12: Electronic band diagram and DOS of 2D Mo_2C under the influence of an E-field strength of $E_z = 2.0 \text{ V/\AA}$.

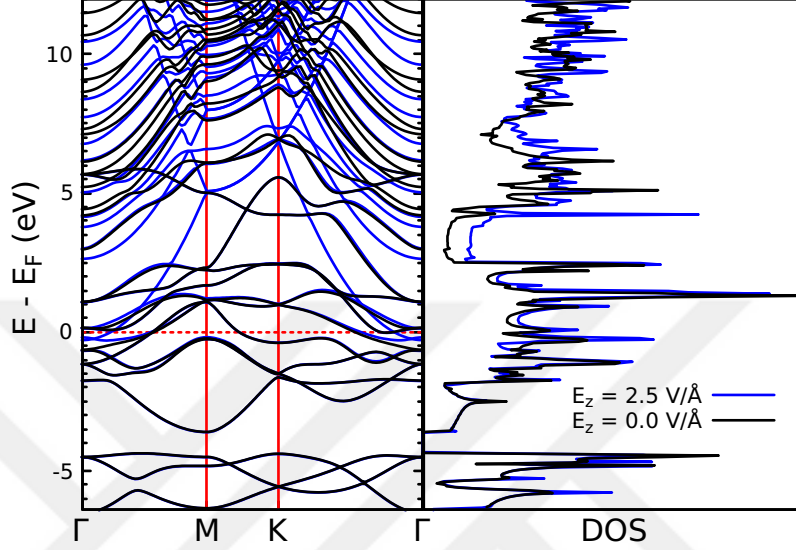
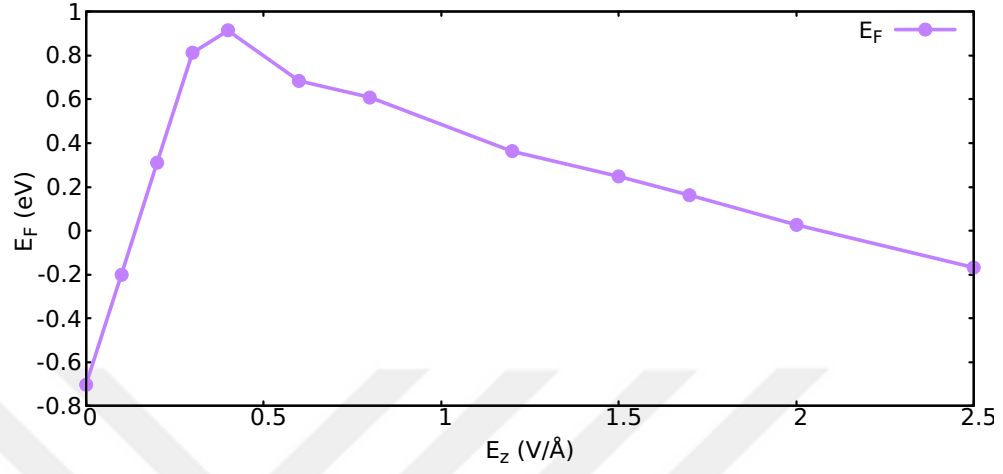
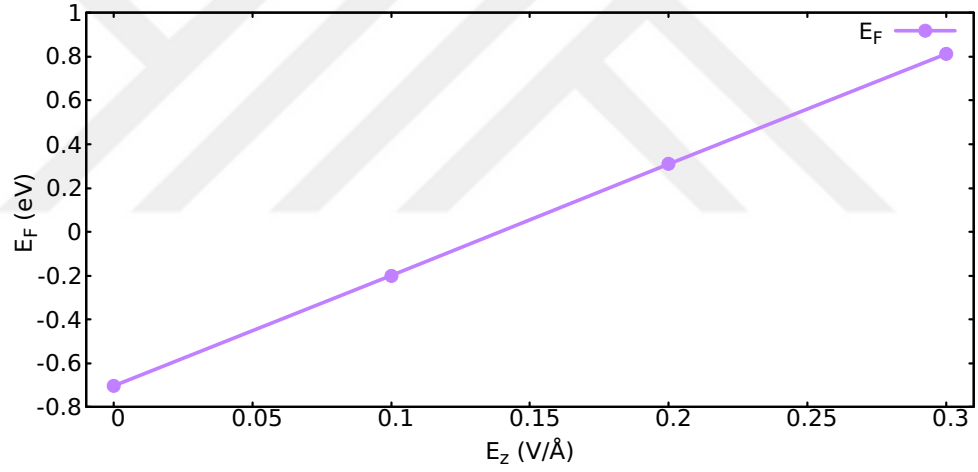


Figure 4.13: Electronic band diagram and DOS of 2D Mo_2C under $E_z=2.5$ V/Å.

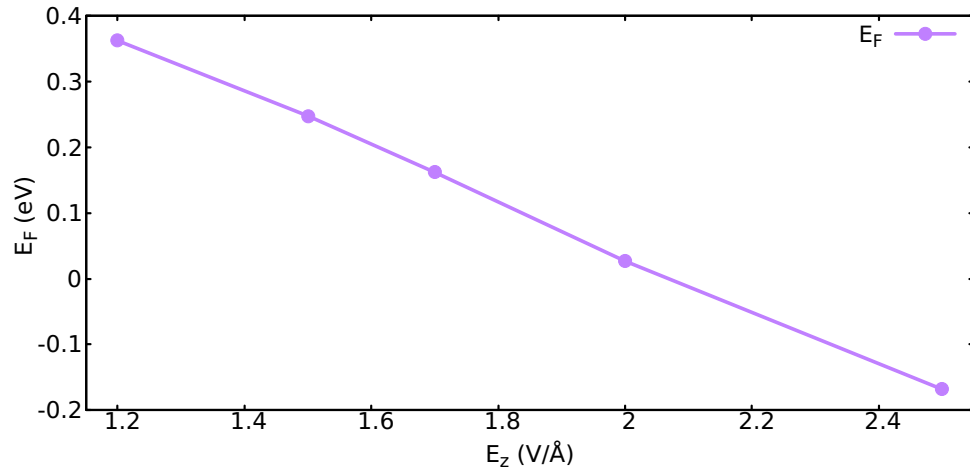
For no-E-case, Fig. 4.1 describes the electronic band structure and DOS plots corresponding to 2D Mo_2C whereas Fig. 4.2 contains electronic band structure and PDOS plots. In the PDOS graph, Mo1 1s indicates that the considered atom is the first molybdenum atom, and the displayed orbital is s-orbital which is the first wave function component. C 2p represents the second wave function component of p-orbital corresponding to the carbon atom et cetera. Conduction band minimum (CBM) contains contributions mostly coming from d orbitals of Mo. In contrast, the major contribution for the valence band maximum (VBM) comes from the s orbital of Mo and there are also contributions due to s and p orbitals of C. The band around -1.75 eV corresponds to d orbitals, the bands between -1.0 eV and -1.5 eV are due to $2s$ orbitals of Mo atoms whereas the bands around -0.5 eV contain Mo $2s$, C $1s$ and C $2p$ contributions. As exhibited in Fig. 4.2, the lowest bands between -4.5 eV and -6.5 eV are due to $2p$ orbitals of the carbon atom. The band at 3 eV is due to the $2p$ orbital of C, the band between 5.0 eV and 5.5 eV corresponds to the carbon $1s$ band.



(a)



(b)



(c)

Figure 4.14: Change in Fermi energy due to various values of E_z . (a) $0.0 \text{ V/Å} \leq E_z \leq 2.5 \text{ V/Å}$. (b) $0.0 \text{ V/Å} \leq E_z \leq 0.3 \text{ V/Å}$. (c) $1.2 \text{ V/Å} \leq E_z \leq 2.5 \text{ V/Å}$.

Due to the perpendicularly applied electric field, E_F shifted as expected. By the SCF calculations, shifts observed in E_F related to the E-field amplitudes are plotted in Fig. 4.14. Similar to the one obtained for monolayer graphene as visualized in Fig. 3.18 in Section 3.1, in the case of monolayer molybdenum carbide, for low strengths of electric field ($0.0 \text{ V/\AA} \leq E_z \leq 0.3 \text{ V/\AA}$) Fermi energy increased linearly. However, for $E_z \geq 0.4 \text{ V/\AA}$, Fermi energy decreased as indicated in Fig. 4.14a. E_F decreased almost linearly but not perfectly linear when the electric field amplitudes got greater, i.e., in the range of $1.2 \text{ V/\AA} \leq E_z \leq 2.5 \text{ V/\AA}$ as can be seen in Fig. 4.14c. Fermi energy is set to zero for all electronic band structure, PDOS, and DOS plots.

For $E_z \leq 0.5 \text{ V/\AA}$, valance bands are almost degenerate. However, similar to the case of monolayer graphene, for 2D Mo_2C , shifts in CB appeared as the E-field was introduced, starting from $0.1 \text{ V/\AA}$. Changes in DOS plots are apparent for $E_z \geq 0.1 \text{ V/\AA}$, as well. Starting from $E_z = 0.6 \text{ V/\AA}$, degeneracy in VB is broken, and the bands related to Mo-s (s-orbital of Mo atom) started to shift upwards as the strength of the E-field increased.

When $E_z = 0.1 \text{ V/\AA}$, the bands above 3.0 eV which are mostly s and p bands of C started to shift downwards (in the direction towards the Fermi level). Bands at higher energies corresponding to the s-orbitals of Mo atoms shifted downwards, as well.

As the strength of the E-field increased, bands corresponding to the s-orbitals of Mo and C continued shifting downward direction. Additionally, bands due to s and p-orbitals of C shifted downwards towards the Fermi level, as well. Moreover, around 10 eV, Mo-s bands shifted starting from $0.1 \text{ V/\AA}$ E-field amplitude. After $E_z = 0.4 \text{ V/\AA}$, the bands around 7 eV at K point in the fBZ shifted upwards and continued to shift in that direction with increasing amplitudes of the electric field. The last described shift became quite obvious starting from $E_z = 1.2 \text{ V/\AA}$ in Fig. 4.9.

At $E_z = 0.8 \text{ V/\AA}$, the s-band touched the Fermi level and shifted below E_F as the strength of the E-field increased which enabled us to n-dope 2D molybdenum carbide under the vertical static electric field so that the effect of n-doping strengthened proportional to the strength of E-field up to $2.5 \text{ V/\AA}$.

When $E_z = 2.0 \text{ V/\AA}$, in the VB, upward-shifted Mo-s band and downward-shifted Mo-s band coincided at Γ point in the fBZ. At $E_z = 2.5 \text{ V/\AA}$, the upward-shifted Mo-s band got closer to the Fermi level and reached above the downward-shifted Mo-s band at Γ point as displayed in Fig. 4.13.

4.2 Optical Properties

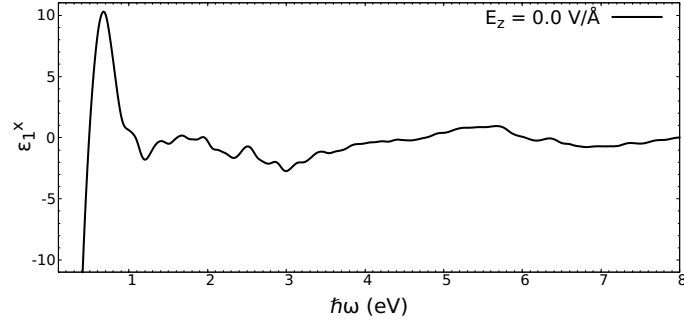
For the optical calculations epsilon.x code is implemented and k-points are used with equal weights with a uniform grid by writing coordinates and equal weights manually using the crystal option. SCF calculations for optical properties are also repeated in the crystal option. The number of manually written coordinates is taken as 576 since the number of k-points along x and y-directions is chosen as 24, and it is chosen as 1 for the z-direction. Gaussian smearing is used for SCF and optical calculations. The same method is used as utilized in Section 3.2, therefore, the same theory applies. To compare the optical properties of 2D molybdenum carbide that we obtained with those calculated in [84], the absorption coefficient $\alpha(\omega)$, and components of real and imaginary parts of the dielectric function have plotted along three spatial directions, i.e., along x, y, and z-directions. In Fig. 4.15 components of ε_1 and ε_2 along x and y-axes, and in Fig. 4.17 x, y, and z-components of the absorption coefficient are plotted. $\alpha(\omega)$ is obtained in terms of ω , the speed of light c , and complex part of the imaginary refractive index $k(\omega)$ as given in Equations 4.1 and 4.2. Together with the perpendicular components of ε_1 and ε_2 , in Fig. 4.16 their horizontal components are calculated by Eq. 3.10 and Eq. 3.11.

$$k(\omega) = \sqrt{\frac{\sqrt{\varepsilon_1^2(\omega) + \varepsilon_2^2(\omega)} - \varepsilon_1(\omega)}{2}} \quad (4.1)$$

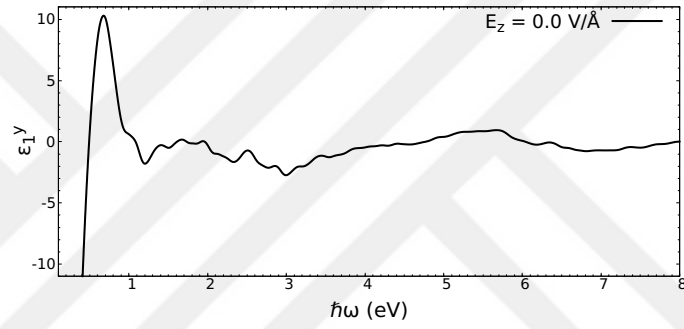
$$\alpha(\omega) = \frac{2\omega k(\omega)}{c} \quad (4.2)$$

From Fig. 4.18 to Fig. 4.28, parallel and perpendicular components of real and imaginary parts of the dielectric function have been exhibited.

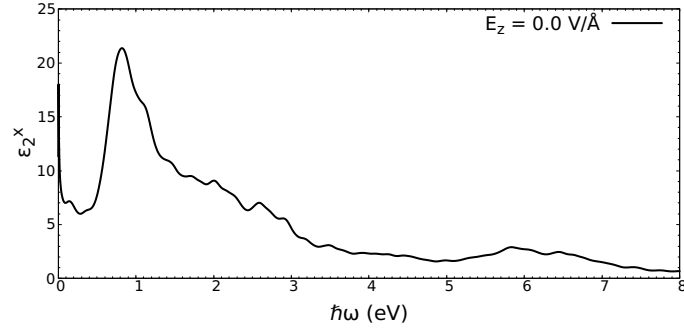
Between Fig. 4.29 and Fig. 4.39, three components of the absorption coefficient have been obtained for all applied E-field strengths.



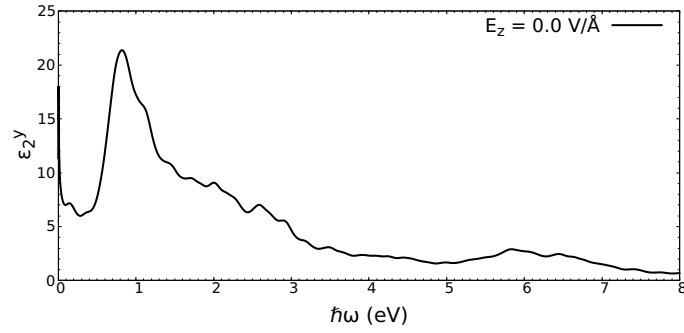
(a)



(b)

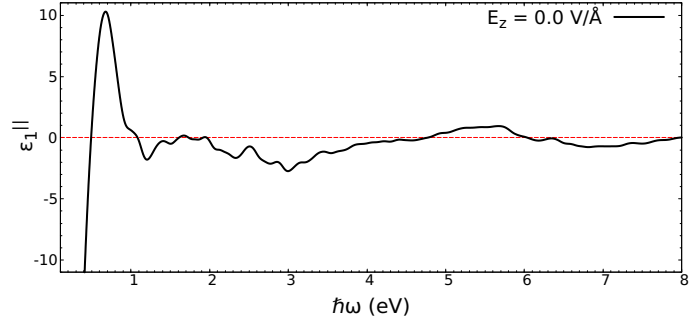


(c)

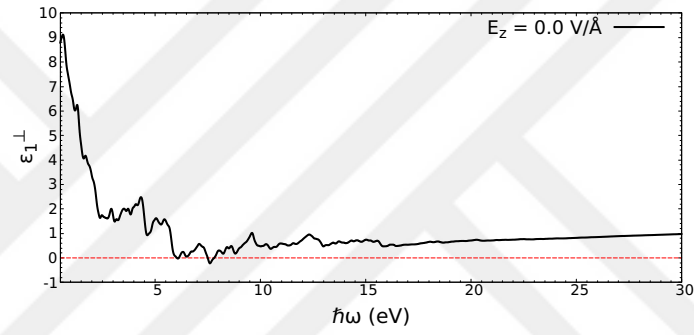


(d)

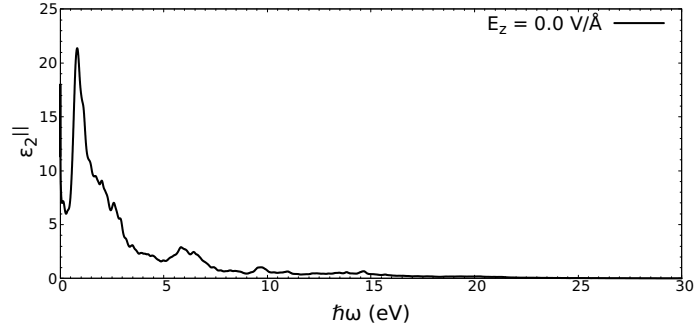
Figure 4.15: For 2D Mo_2C without any external field effects: (a) ε_1^x plot. (b) ε_1^y plot. (c) ε_2^x plot. (d) ε_2^y plot.



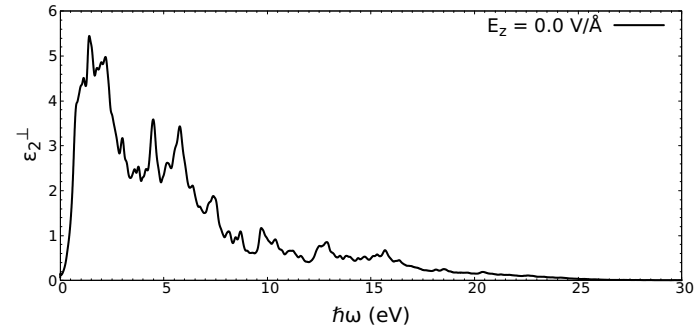
(a)



(b)

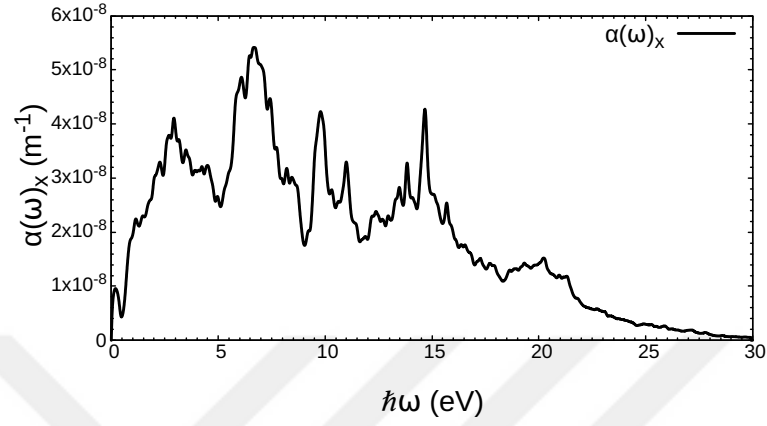


(c)

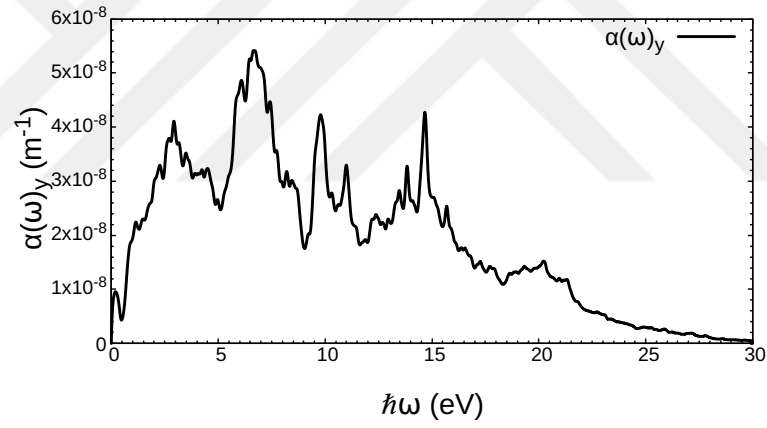


(d)

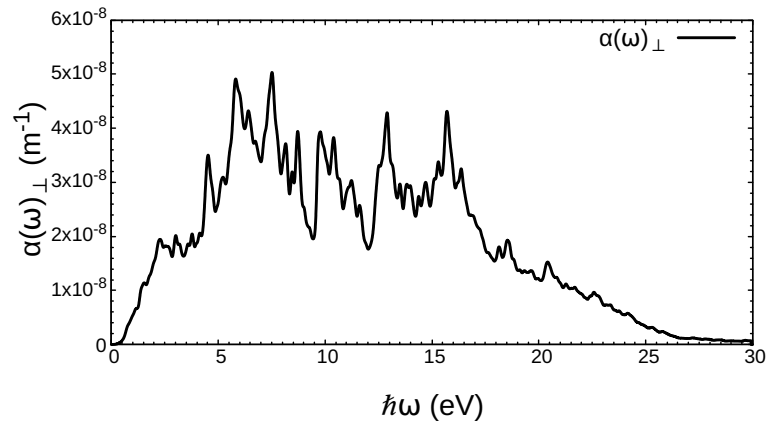
Figure 4.16: For 2D Mo_2C without any external field effects: (a) $\varepsilon_1^{\parallel}$ plot. (b) $\varepsilon_1^{\perp}$ plot. (c) $\varepsilon_2^{\parallel}$ plot. (d) $\varepsilon_2^{\perp}$ plot.



(a)

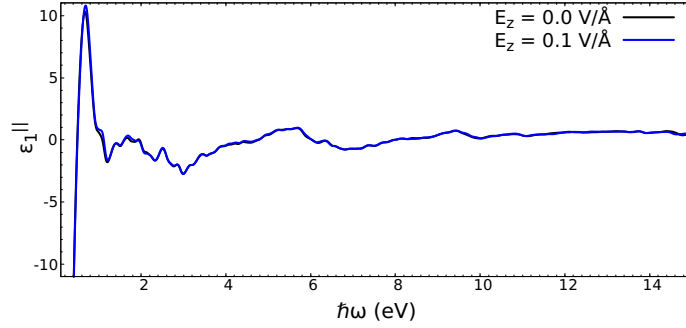


(b)

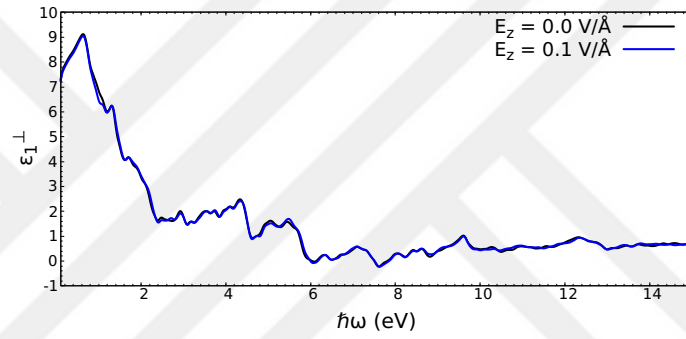


(c)

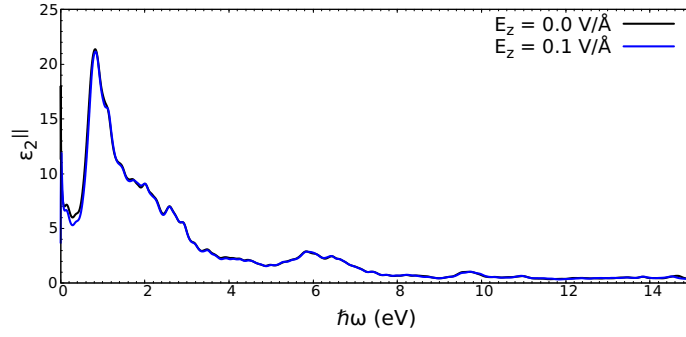
Figure 4.17: For monolayer Mo_2C without any external field effects: (a) $\alpha(\omega)_x$ plot. (b) $\alpha(\omega)_y$ plot. (c) $\alpha(\omega)_z$ plot.



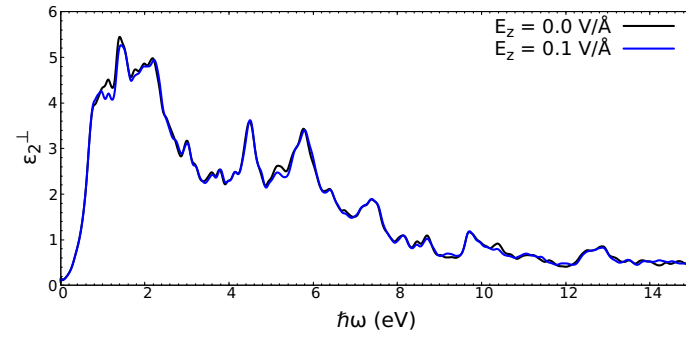
(a)



(b)

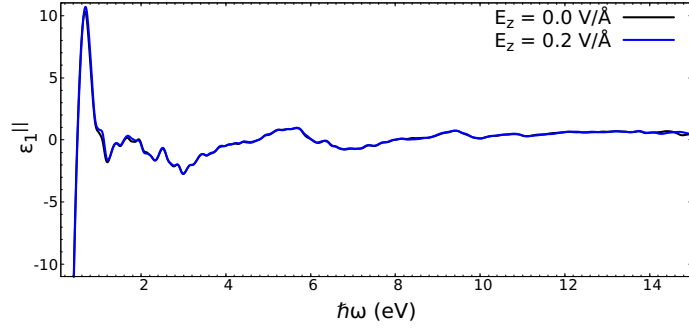


(c)

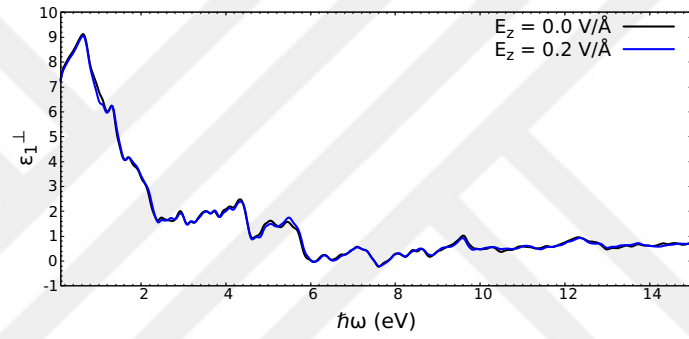


(d)

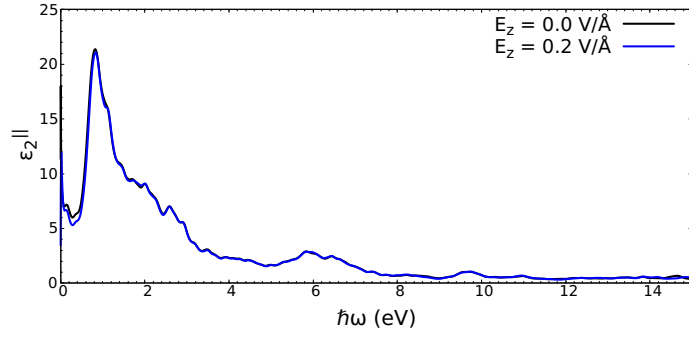
Figure 4.18: Dielectric function data under the perpendicular E-field of strength $E_z=0.1$ V/Å: (a) $\epsilon_1^{\parallel}$ plot. (b) $\epsilon_1^{\perp}$ plot. (c) $\epsilon_2^{\parallel}$ plot. (d) $\epsilon_2^{\perp}$ plot.



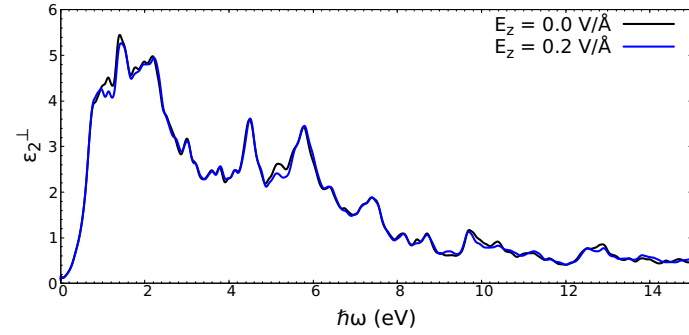
(a)



(b)

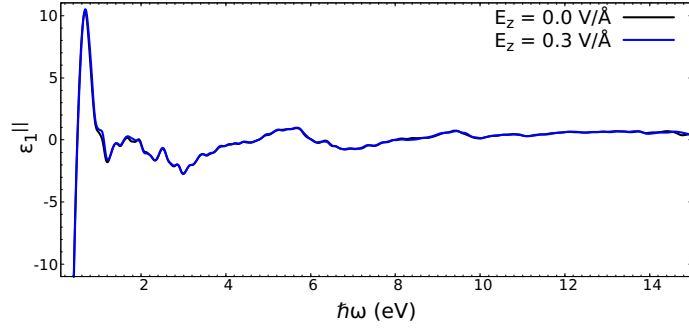


(c)

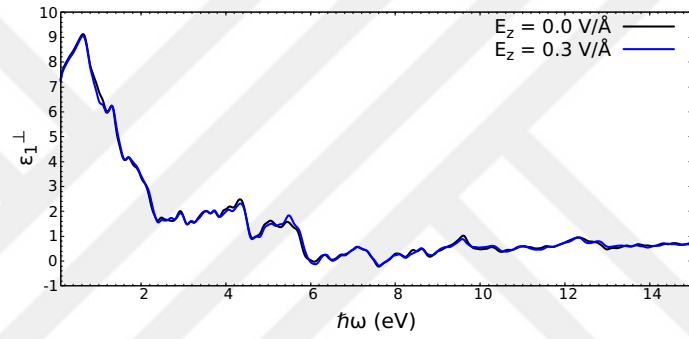


(d)

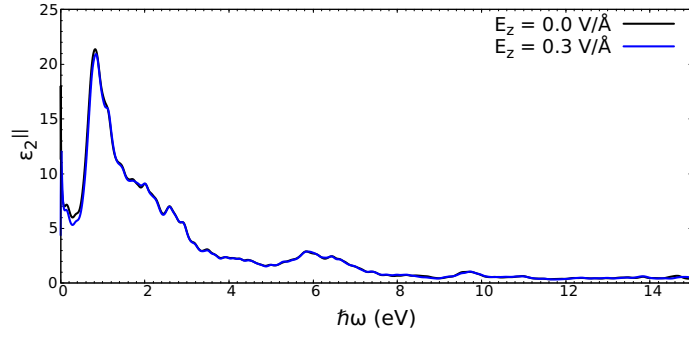
Figure 4.19: Dielectric function data in the presence of an E-field of strength $E_z=0.2$ V/Å: (a) $\epsilon_1^{\parallel}$ plot. (b) $\epsilon_1^{\perp}$ plot. (c) $\epsilon_2^{\parallel}$ plot. (d) $\epsilon_2^{\perp}$ plot.



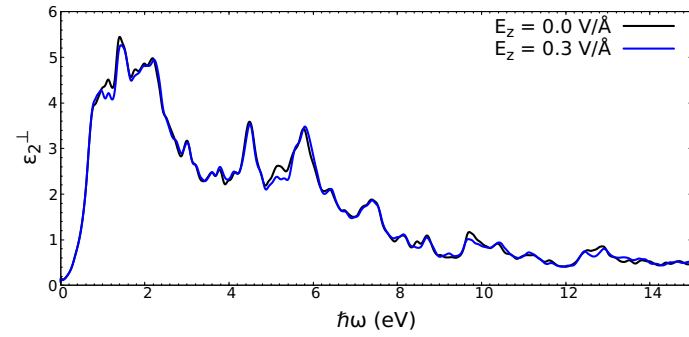
(a)



(b)

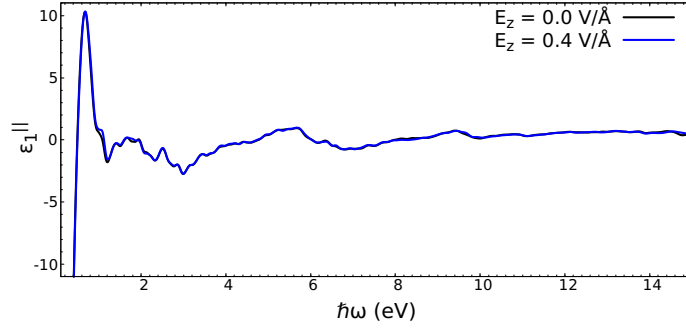


(c)

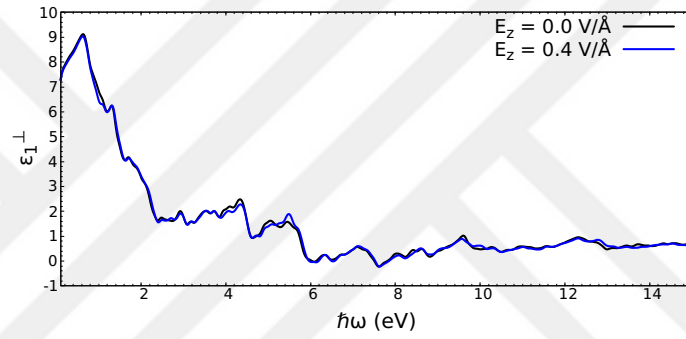


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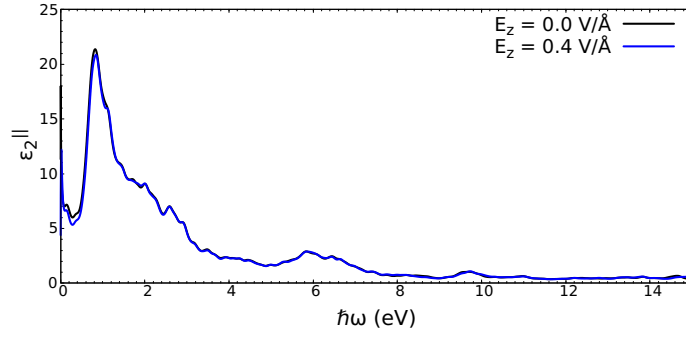
Figure 4.20: Dielectric function data under the perpendicular E-field strength of $E_z=0.3$ V/Å: (a) $\epsilon_1^{\parallel}$ plot. (b) $\epsilon_1^{\perp}$ plot. (c) $\epsilon_2^{\parallel}$ plot. (d) $\epsilon_2^{\perp}$ plot.



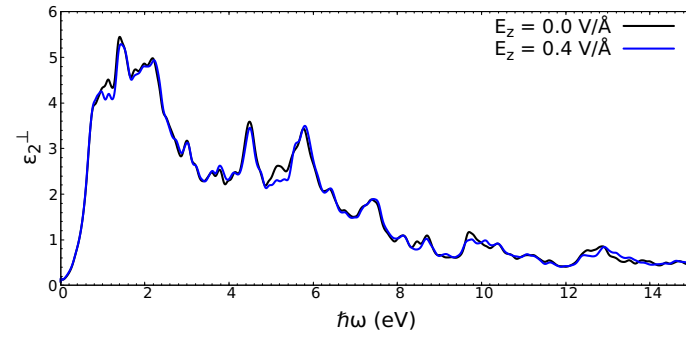
(a)



(b)

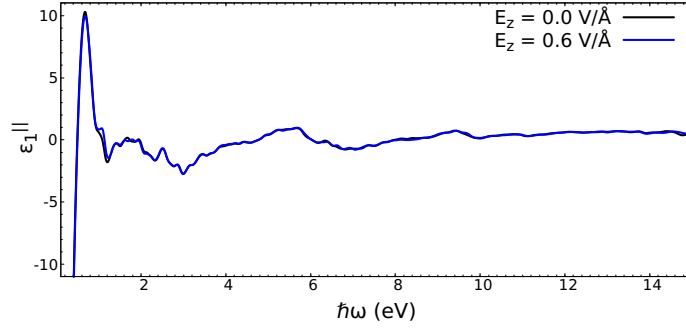


(c)

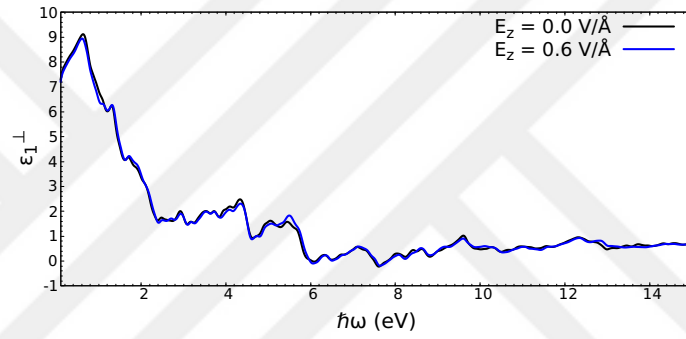


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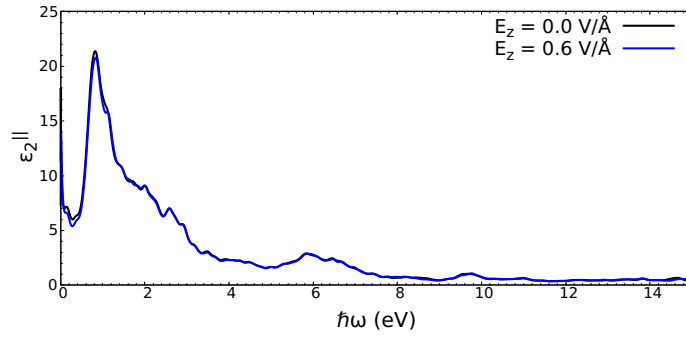
Figure 4.21: Dielectric function data in the presence of an E-field of strength $E_z=0.4$ V/Å: (a) $\epsilon_1^{\parallel}$ plot. (b) $\epsilon_1^{\perp}$ plot. (c) $\epsilon_2^{\parallel}$ plot. (d) $\epsilon_2^{\perp}$ plot.



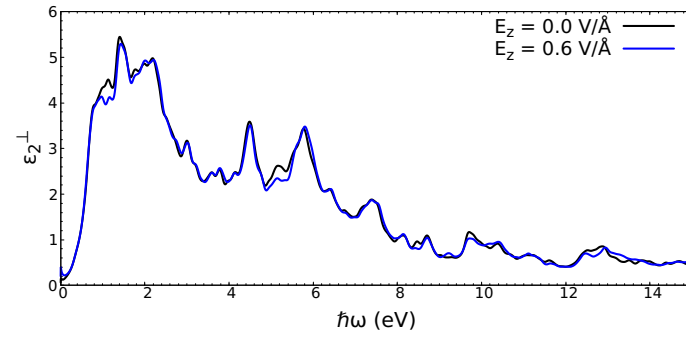
(a)



(b)

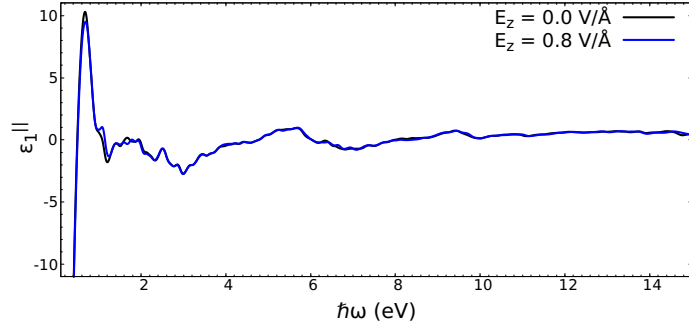


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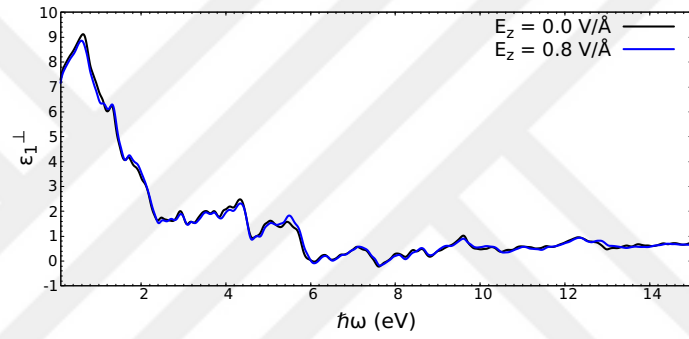


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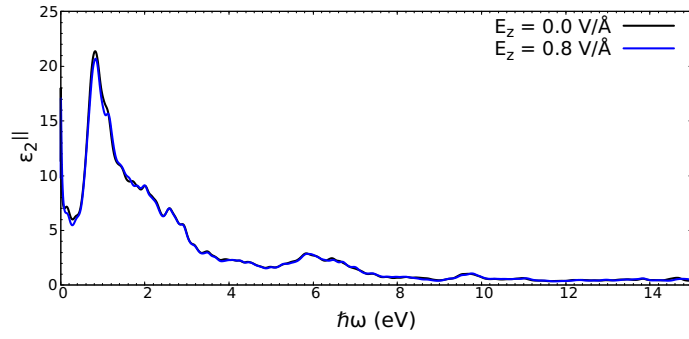
Figure 4.22: Dielectric function data under $E_z=0.6 \text{ V/\AA}$: (a) $\varepsilon_1^{\parallel}$ plot. (b) $\varepsilon_1^{\perp}$ plot. (c) $\varepsilon_2^{\parallel}$ plot. (d) $\varepsilon_2^{\perp}$ plot.



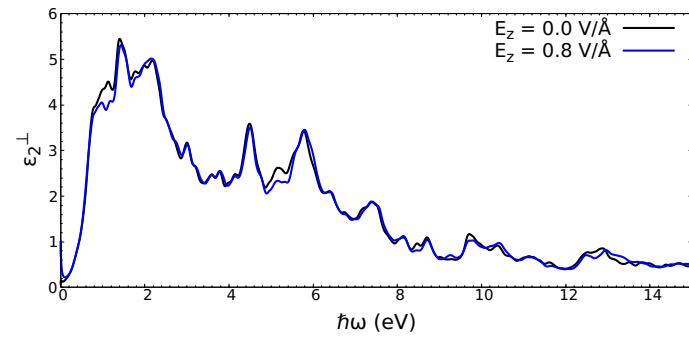
(a)



(b)

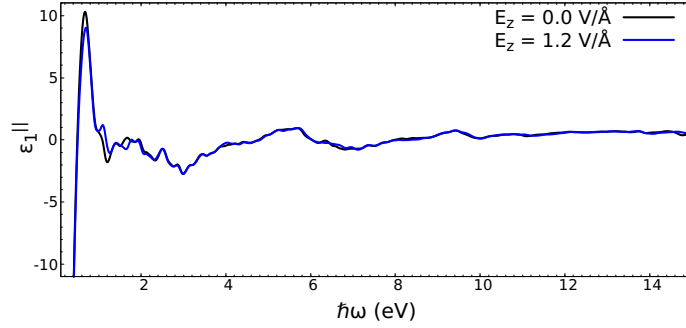


(c)

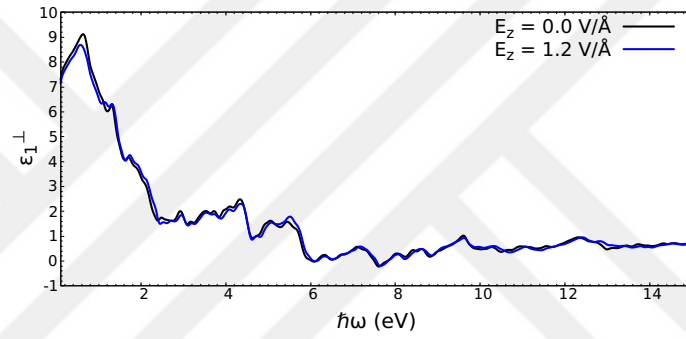


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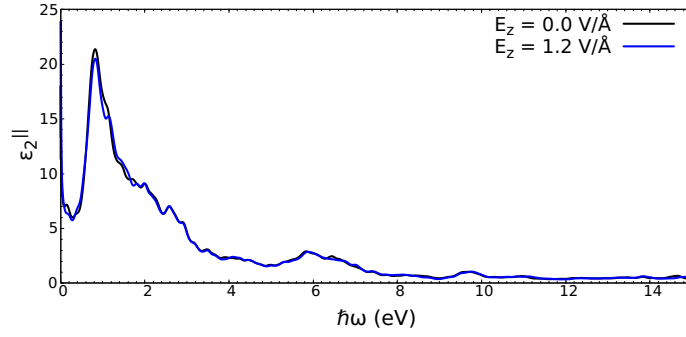
Figure 4.23: Dielectric function data under the perpendicular E-field applied with a strength of $E_z=0.8$ V/Å: (a) $\varepsilon_1^{\parallel}$ plot. (b) $\varepsilon_1^{\perp}$ plot. (c) $\varepsilon_2^{\parallel}$ plot. (d) $\varepsilon_2^{\perp}$ plot.



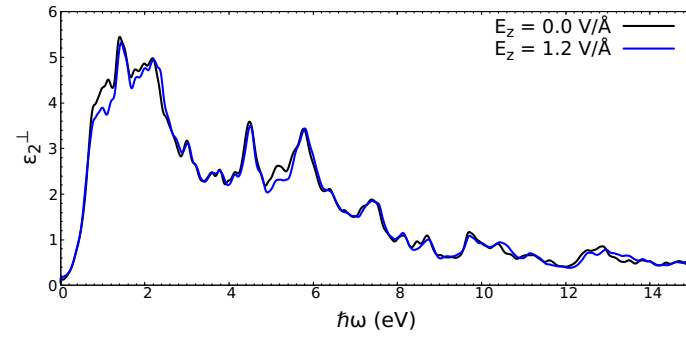
(a)



(b)

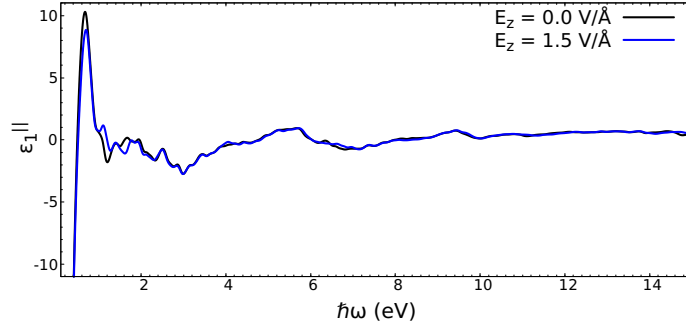


(c)

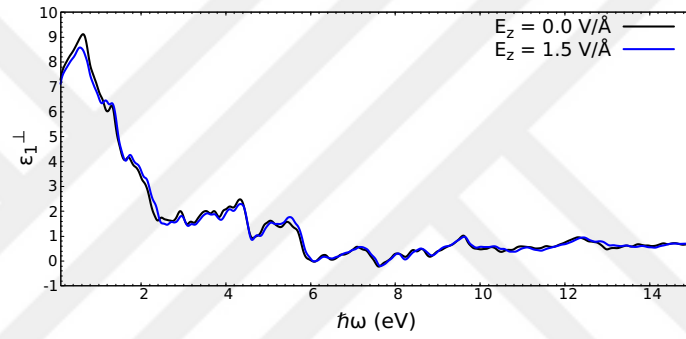


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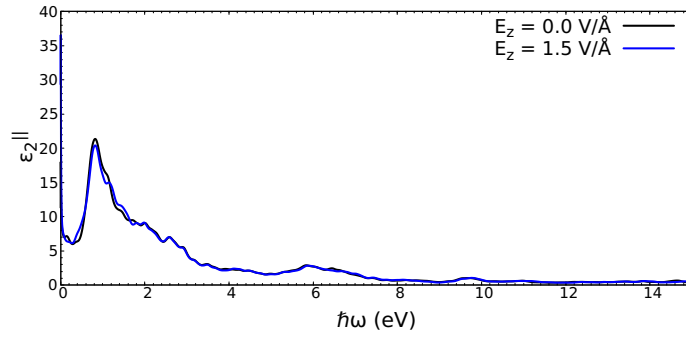
Figure 4.24: Dielectric function data under an E-field of magnitude $E_z=1.2 \text{ V/\AA}$:
(a) $\varepsilon_1^{\parallel}$ plot. (b) $\varepsilon_1^{\perp}$ plot. (c) $\varepsilon_2^{\parallel}$ plot. (d) $\varepsilon_2^{\perp}$ plot.



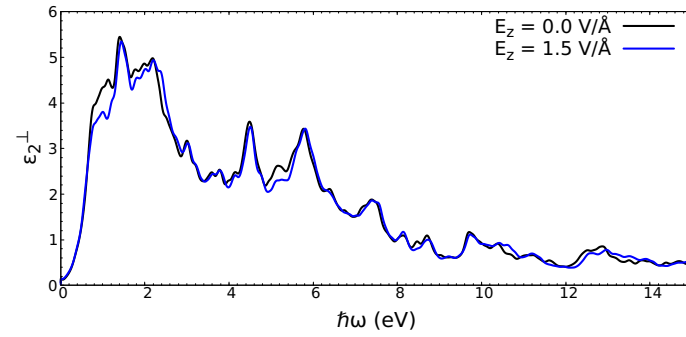
(a)



(b)

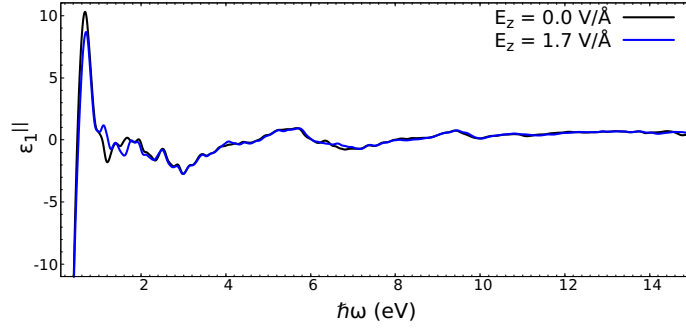


(c)

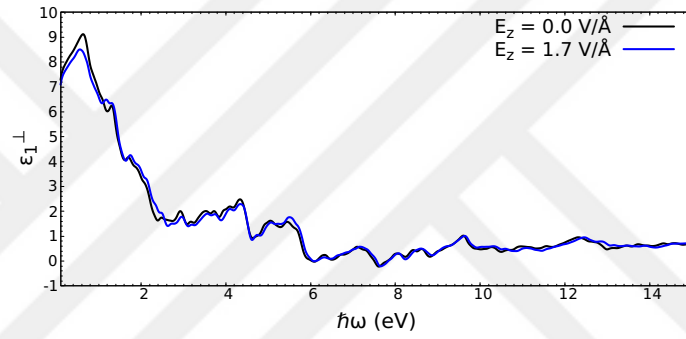


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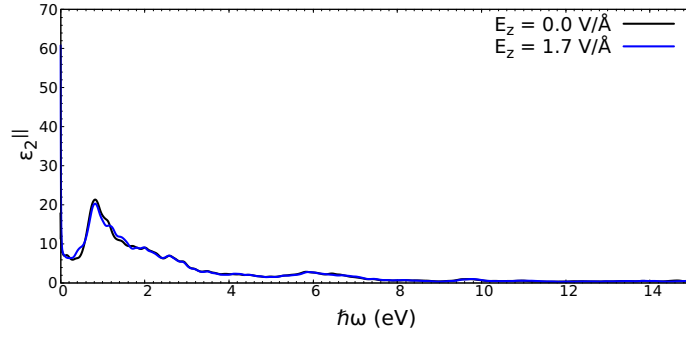
Figure 4.25: Dielectric function data in the presence of an E-field of strength $E_z=1.5$ V/Å: (a) $\epsilon_1^{\parallel}$ plot. (b) $\epsilon_1^{\perp}$ plot. (c) $\epsilon_2^{\parallel}$ plot. (d) $\epsilon_2^{\perp}$ plot.



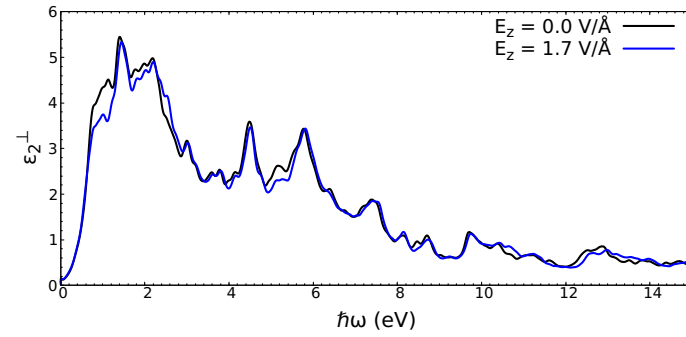
(a)



(b)

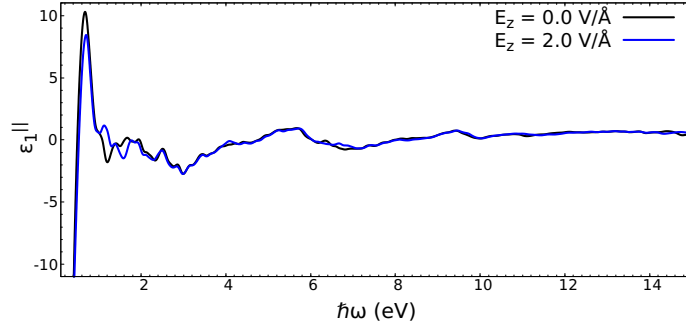


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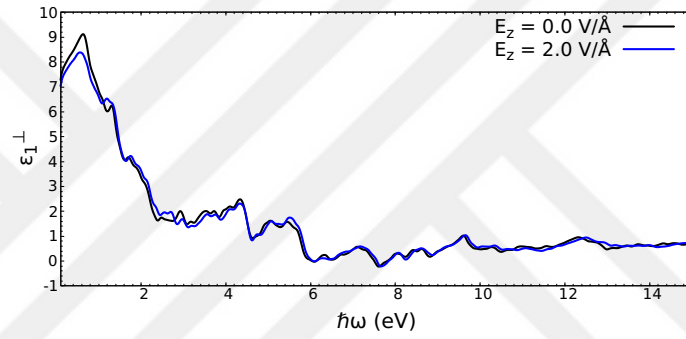


(d)

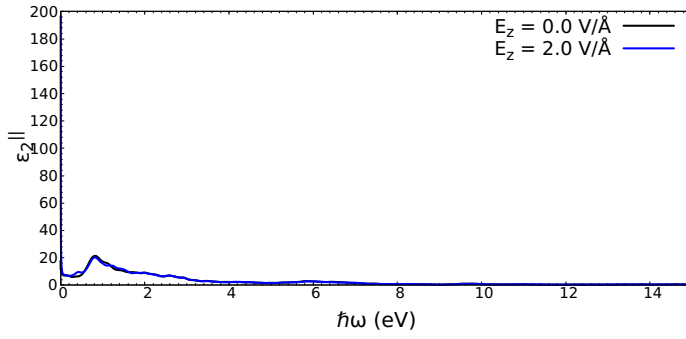
Figure 4.26: Dielectric function data under the influence of an E-field of strength $E_z=1.7$ V/Å: (a) $\epsilon_1^{\parallel}$ plot. (b) $\epsilon_1^{\perp}$ plot. (c) $\epsilon_2^{\parallel}$ plot. (d) $\epsilon_2^{\perp}$ plot.



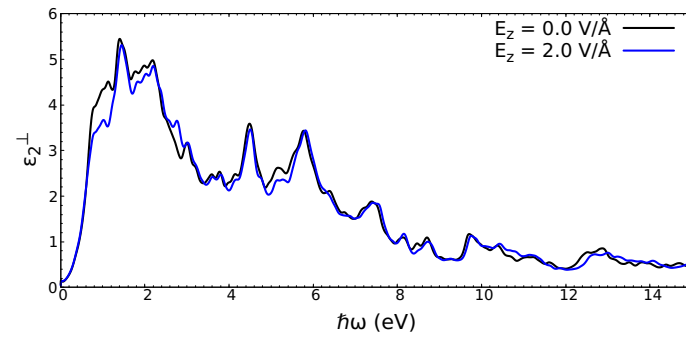
(a)



(b)

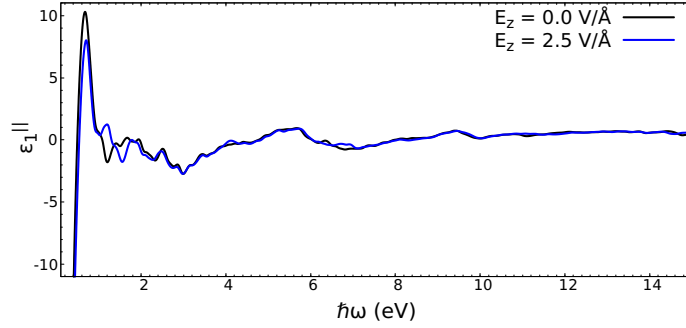


(c)

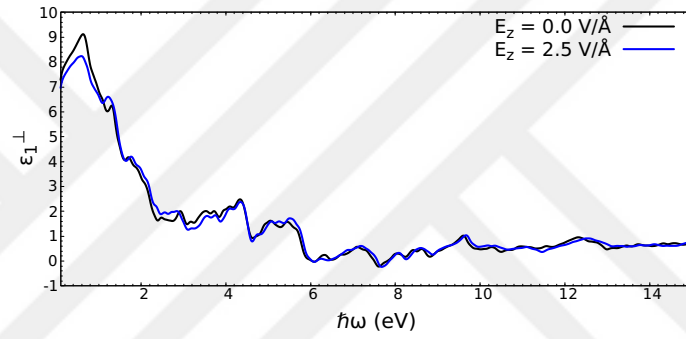


(d)

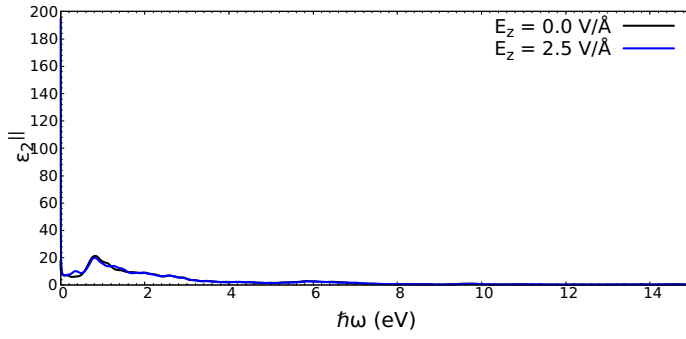
Figure 4.27: Dielectric function data under the influence of an E-field magnitude of $E_z=2.0$ V/Å: (a) $\varepsilon_1^{\parallel}$ plot. (b) $\varepsilon_1^{\perp}$ plot. (c) $\varepsilon_2^{\parallel}$ plot. (d) $\varepsilon_2^{\perp}$ plot.



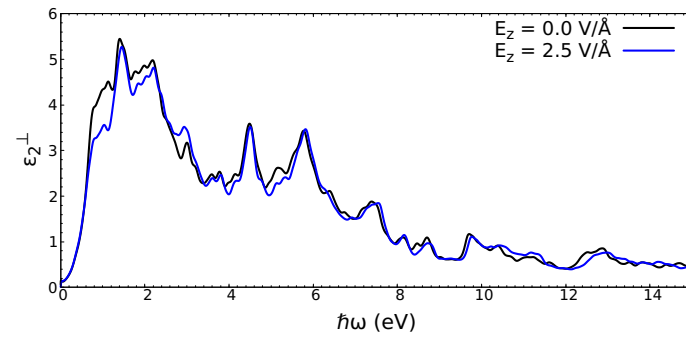
(a)



(b)



(c)

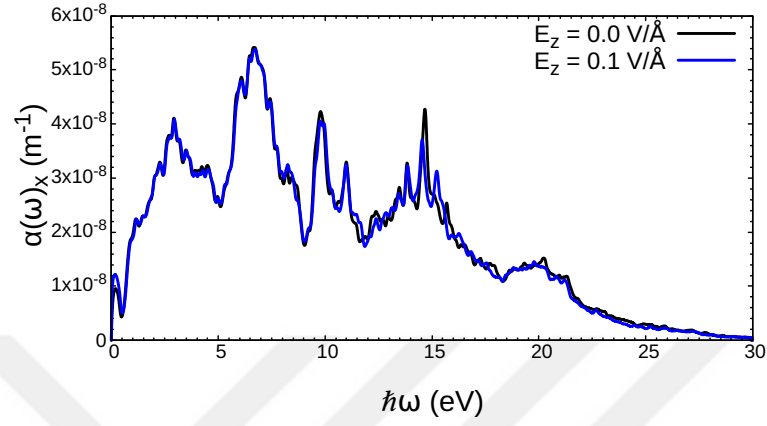


(d)

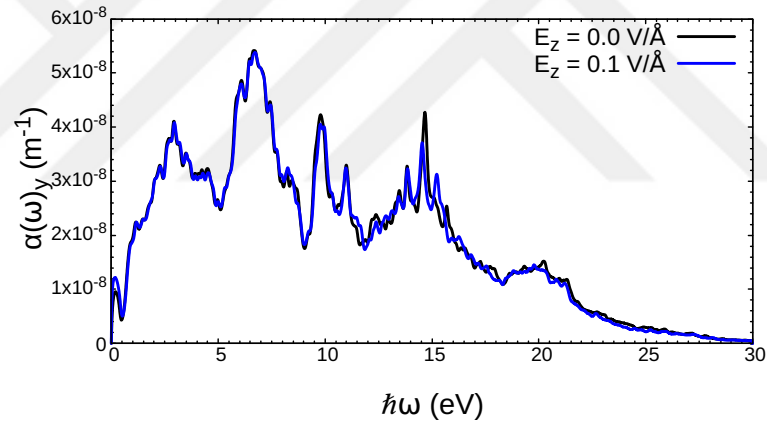
Figure 4.28: Dielectric function data when the perpendicularly applied E-field magnitude is $E_z=2.5$ V/Å: (a) $\epsilon_1^{\parallel}$ plot. (b) $\epsilon_1^{\perp}$ plot. (c) $\epsilon_2^{\parallel}$ plot. (d) $\epsilon_2^{\perp}$ plot.

No significant changes were observed in ε_1 and ε_2 up to $E_z=0.4$ V/Å, however, there are small decreases in the amplitudes of the peaks at 1 eV and 5 eV corresponds to $\varepsilon_2^\perp$ data under the vertical electric field. In $\varepsilon_1^\perp$ plot the peak around 0.9 eV started decreasing after $E_z=0.6$ V/Å and decreased more by increasing E-field strengths. Starting from 1.5 V/Å E-field amplitude, $\varepsilon_1^\perp$ curve between 1.8 eV and 6 eV blueshifted as demonstrated in Fig. 4.25b. Additionally, by increasing magnitudes of the E-field, the point where the imaginary component of the dielectric function in the horizontal direction of polarization cuts the perpendicular axis at higher points. Starting with $E_z=0.8$ V/Å, $\varepsilon_2^\perp$ curve at higher energy zone (after 10 eV) blueshifted. By increasing E-field strength, the amplitude of the first peak around 1 eV in $\varepsilon_2^\perp$ plot kept decreasing.

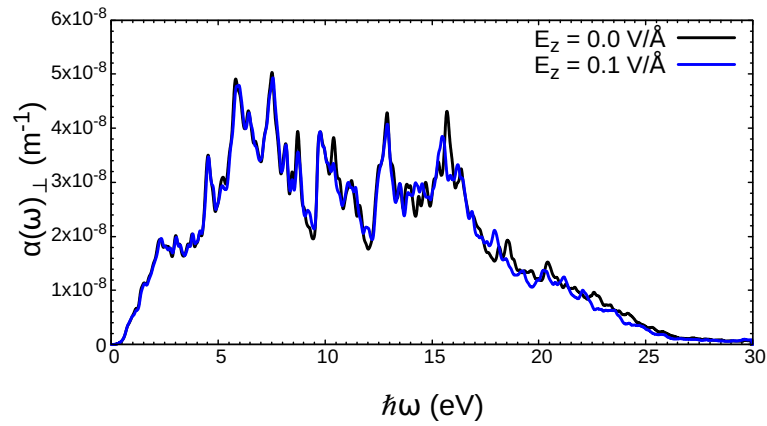
For the absorption coefficient plots, in the lower energy zone (below 5 eV) amplitudes of the peaks grew with increasing amplitudes of the E-field in each direction. Between 5.5 eV and 12 eV peaks blueshifted along x, y, and z-directions. Moreover, for the vertical component of the absorption coefficient, blueshift was observed between 10-15 eV after $E_z=0.8$ V/Å. For the greater values of E-field amplitudes up to $E_z=2.0$ V/Å (Fig. 4.38), x, and y-components of the absorption coefficient also blueshifted between 10-15 eV. Unlike monolayer graphene, there were no additional peaks in the dielectric function spectra with the effect of E-field.



(a)

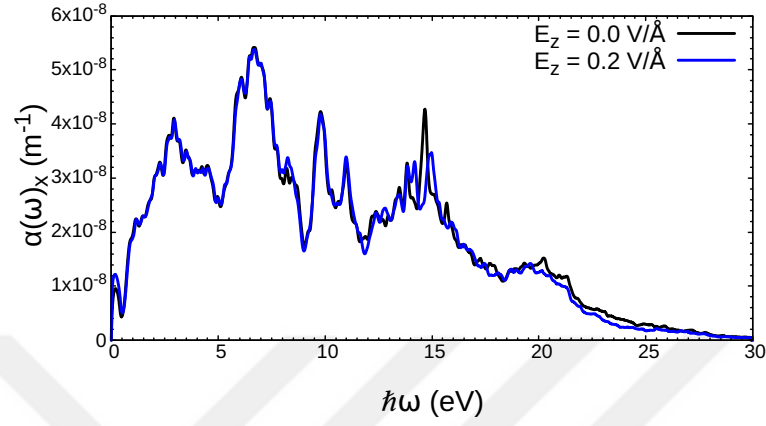


(b)

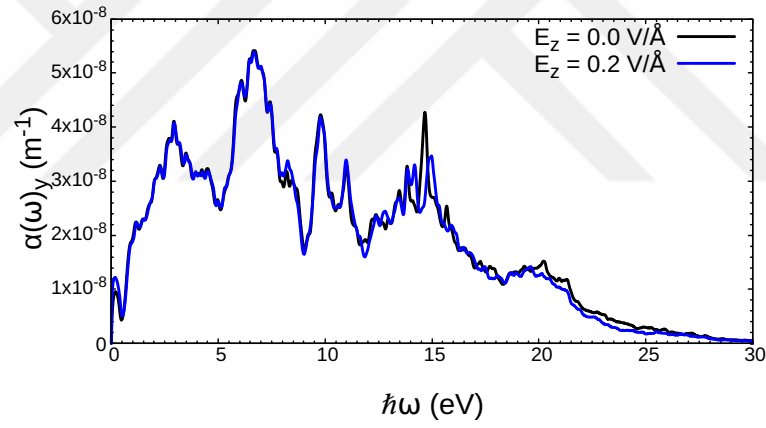


(c)

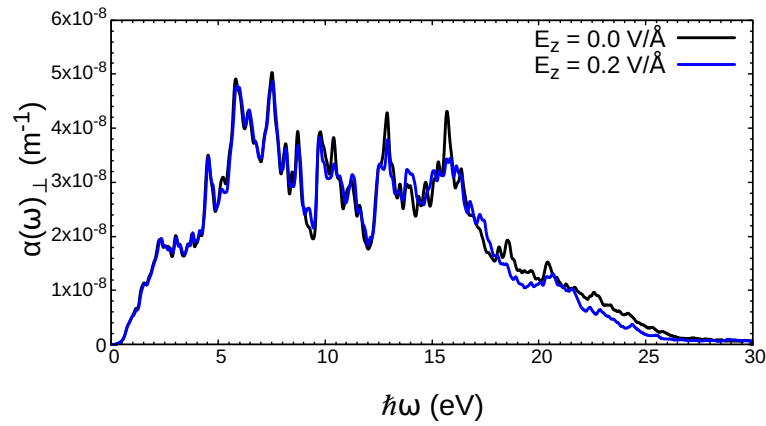
Figure 4.29: For monolayer Mo_2C in the presence of an E-field of strength $E_z=0.1$ V/Å (a) $\alpha(\omega)_x$ plot. (b) $\alpha(\omega)_y$ plot. (c) $\alpha(\omega)_z$ plot.



(a)

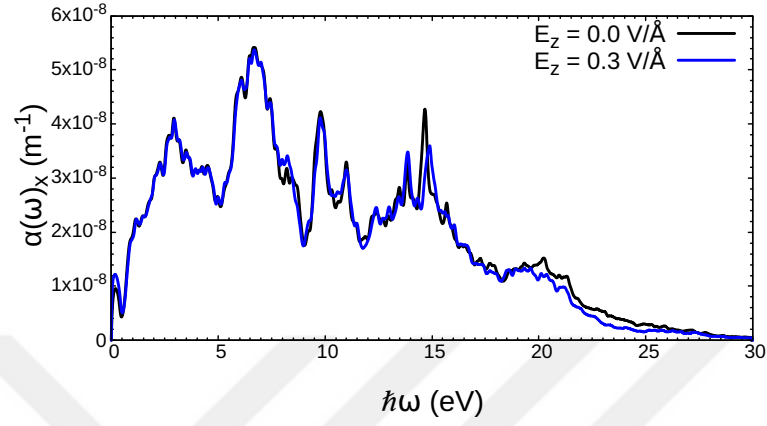


(b)

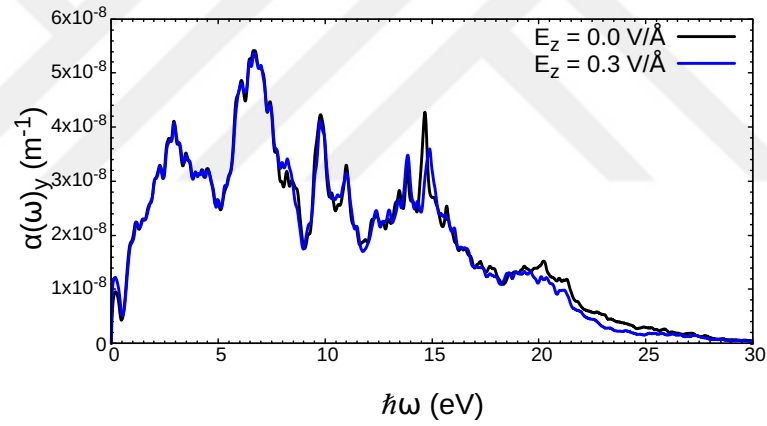


(c)

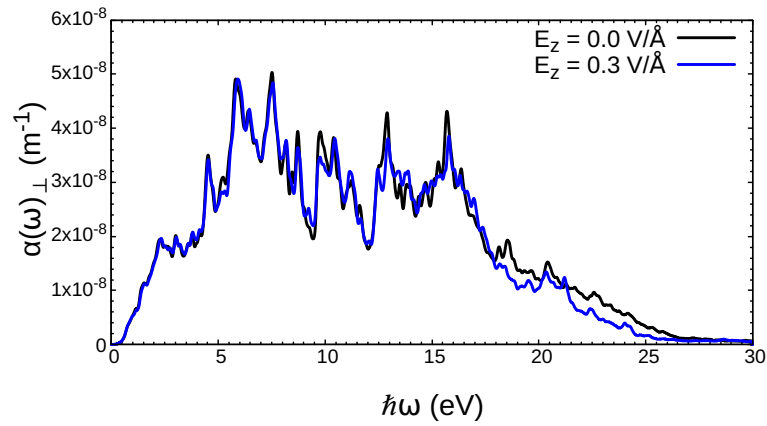
Figure 4.30: For monolayer Mo_2C under the perpendicular E-field applied with a strength of $E_z=0.2$ V/Å (a) $\alpha(\omega)_x$ plot. (b) $\alpha(\omega)_y$ plot. (c) $\alpha(\omega)_z$ plot.



(a)

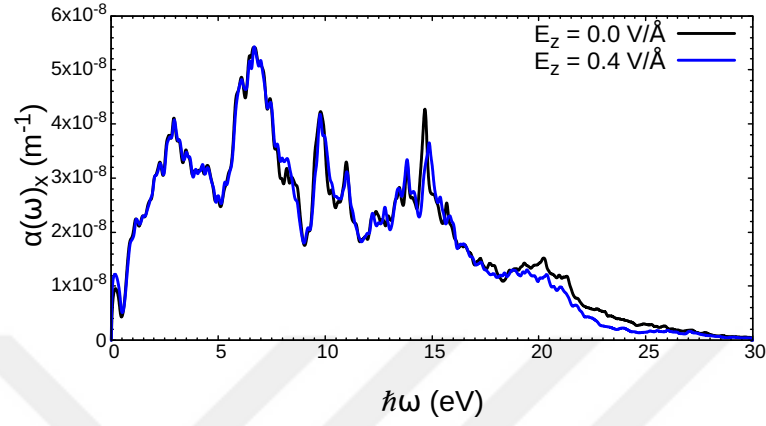


(b)

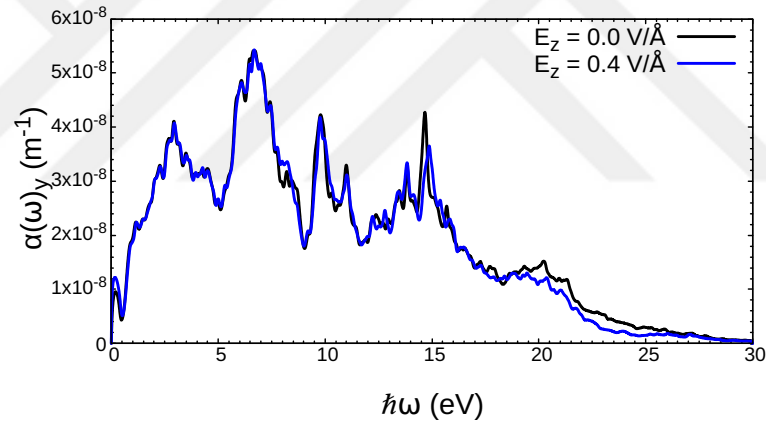


(c)

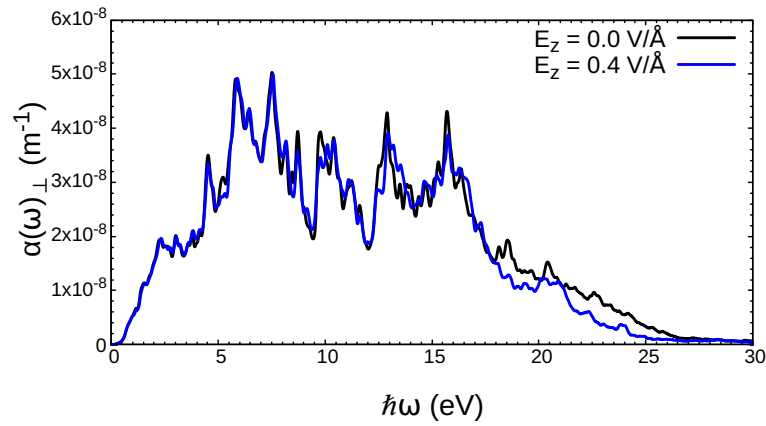
Figure 4.31: For monolayer Mo_2C under $E_z=0.3$ V/Å (a) $\alpha(\omega)_x$ plot. (b) $\alpha(\omega)_y$ plot. (c) $\alpha(\omega)_z$ plot.



(a)

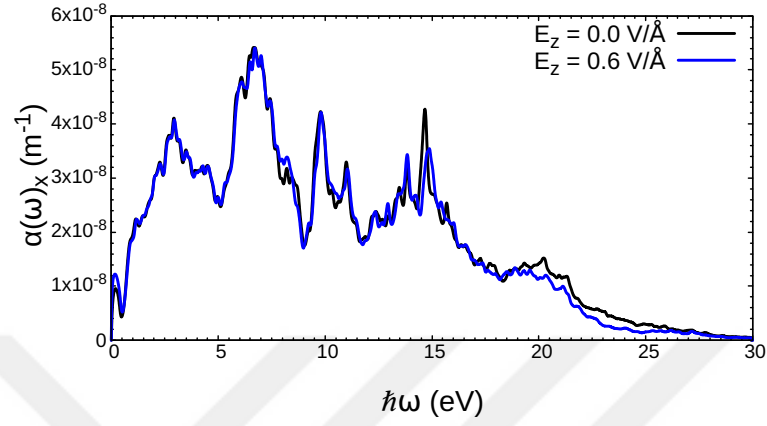


(b)

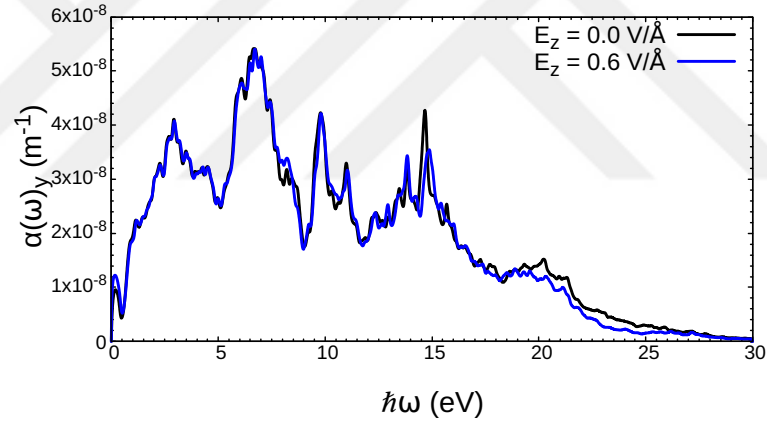


(c)

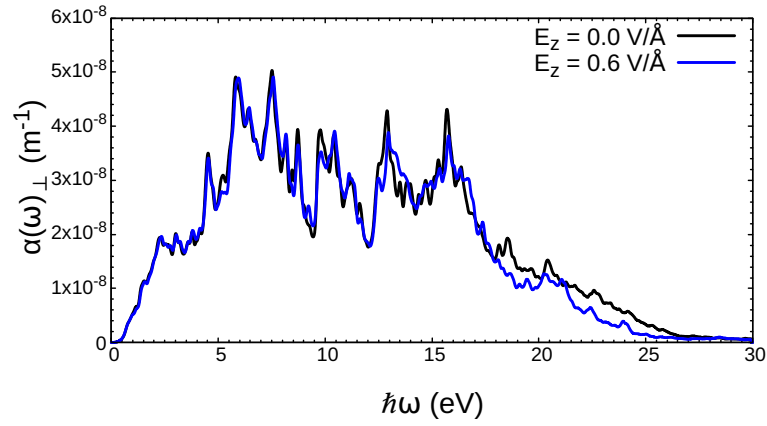
Figure 4.32: For monolayer Mo_2C in the presence of an E-field of strength $E_z=0.4$ V/Å (a) $\alpha(\omega)_x$ plot. (b) $\alpha(\omega)_y$ plot. (c) $\alpha(\omega)_z$ plot.



(a)

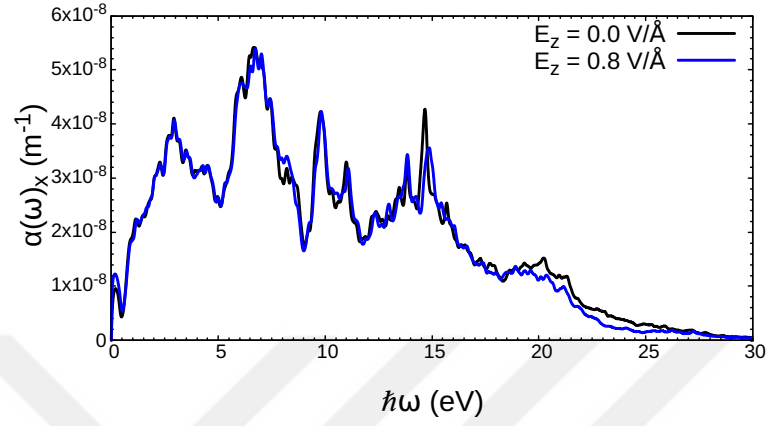


(b)

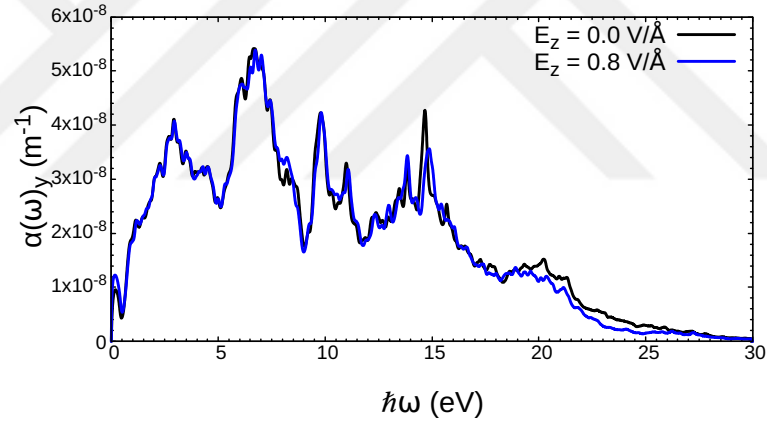


(c)

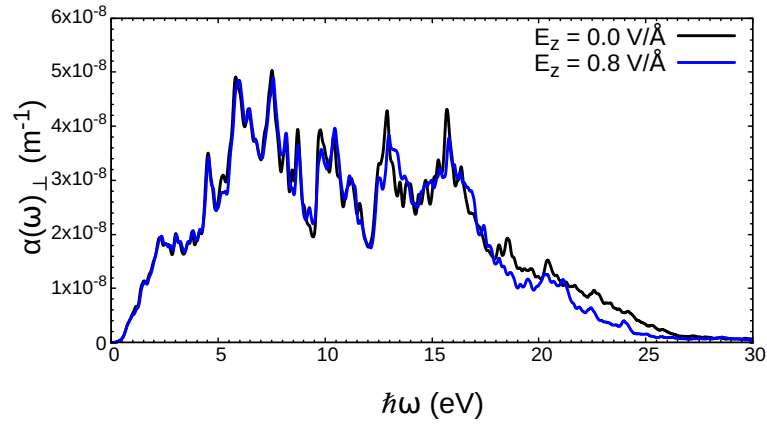
Figure 4.33: For monolayer Mo_2C under the influence of an E-field magnitude of $E_z=0.6$ V/Å (a) $\alpha(\omega)_x$ plot. (b) $\alpha(\omega)_y$ plot. (c) $\alpha(\omega)_z$ plot.



(a)

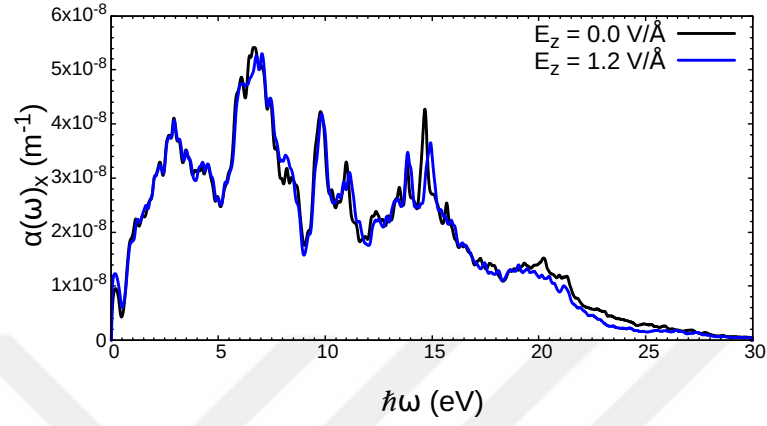


(b)

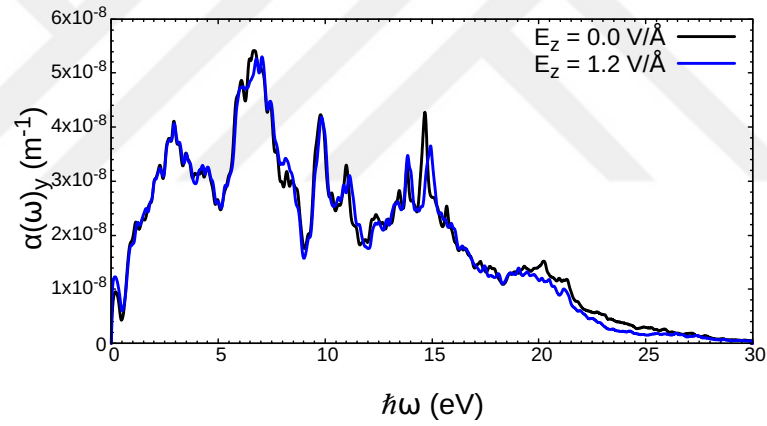


(c)

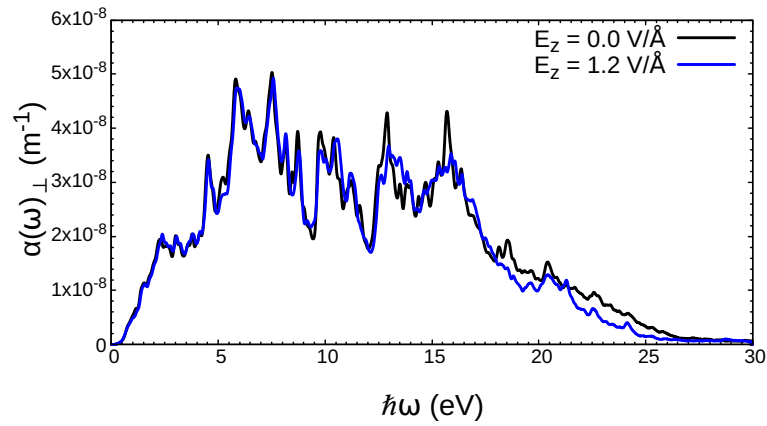
Figure 4.34: For monolayer Mo_2C in the presence of an E-field of strength $E_z=0.8$ V/Å (a) $\alpha(\omega)_x$ plot. (b) $\alpha(\omega)_y$ plot. (c) $\alpha(\omega)_z$ plot.



(a)

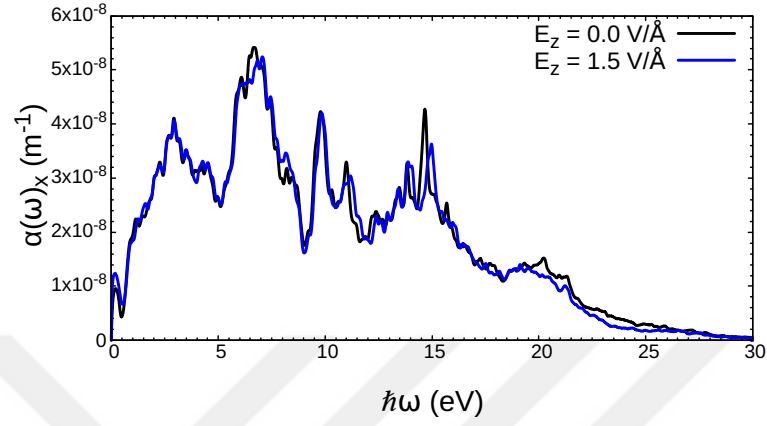


(b)

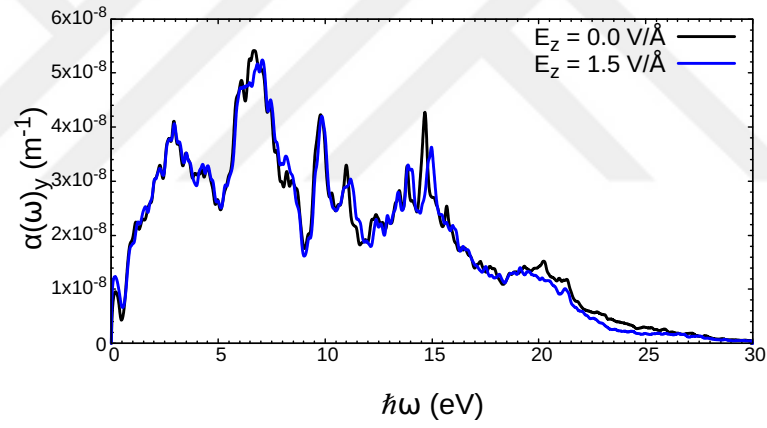


(c)

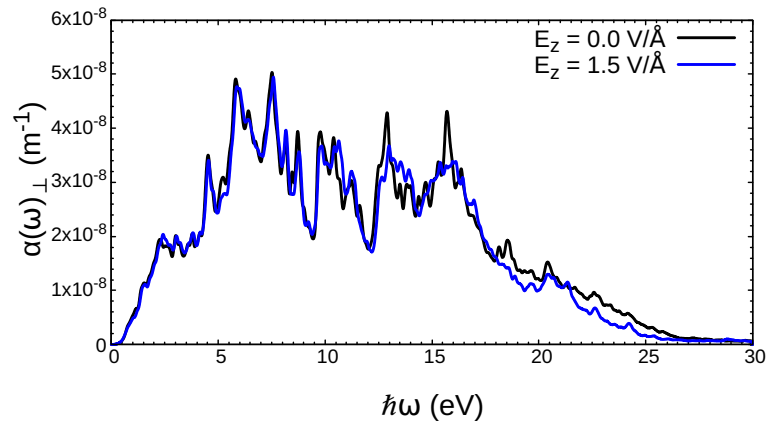
Figure 4.35: For monolayer Mo_2C under the influence of $E_z=1.2$ V/Å (a) $\alpha(\omega)_x$ plot. (b) $\alpha(\omega)_y$ plot. (c) $\alpha(\omega)_z$ plot.



(a)

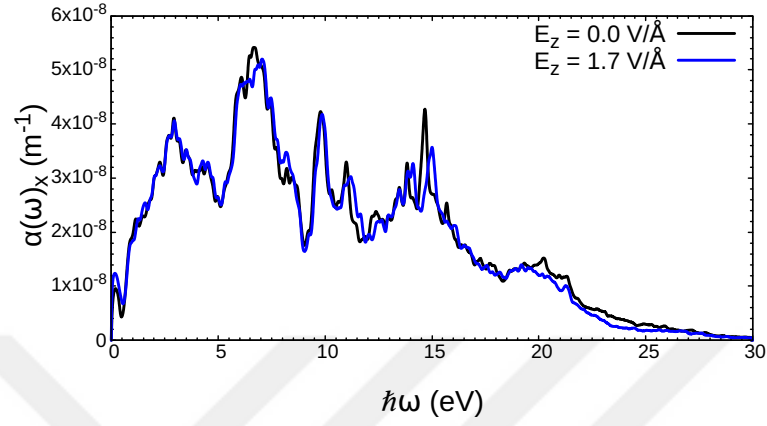


(b)

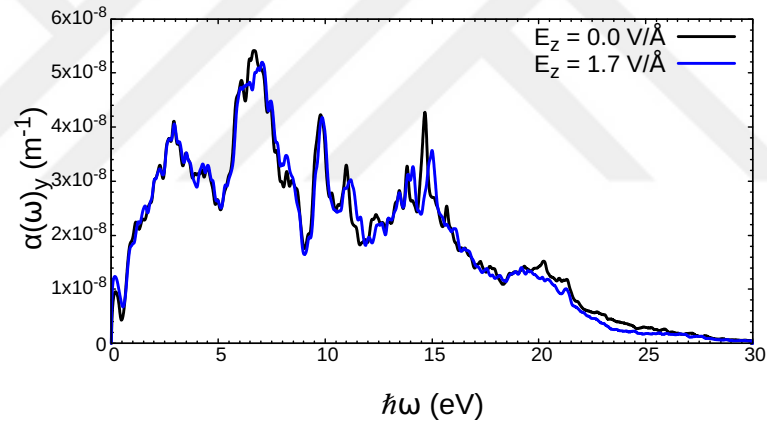


(c)

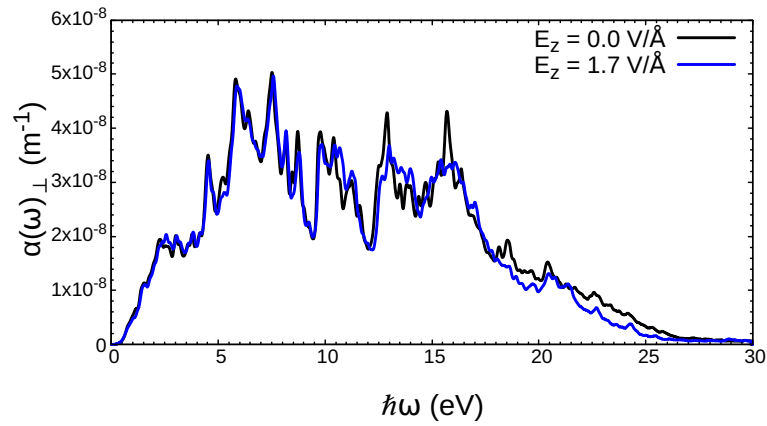
Figure 4.36: For monolayer Mo_2C in the presence of an E-field of strength $E_z=1.5$ V/Å (a) $\alpha(\omega)_x$ plot. (b) $\alpha(\omega)_y$ plot. (c) $\alpha(\omega)_z$ plot.



(a)

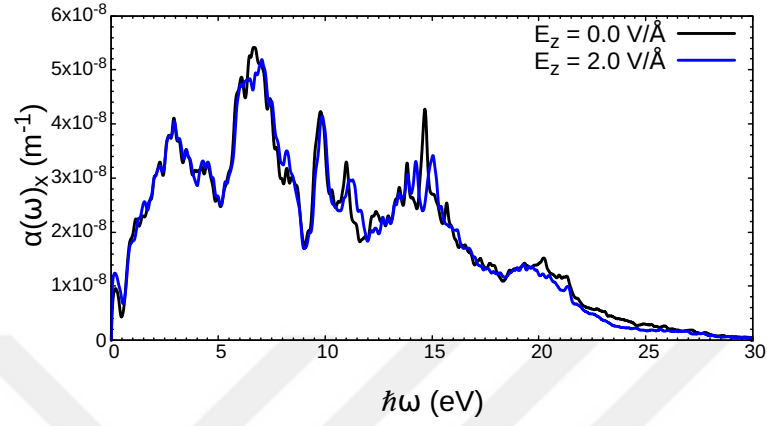


(b)

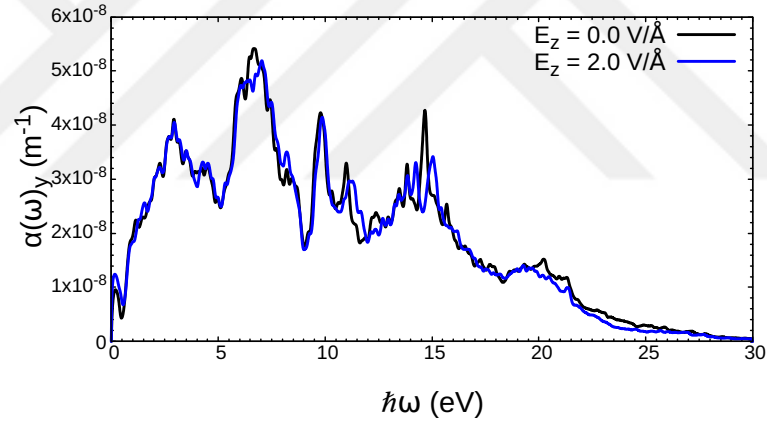


(c)

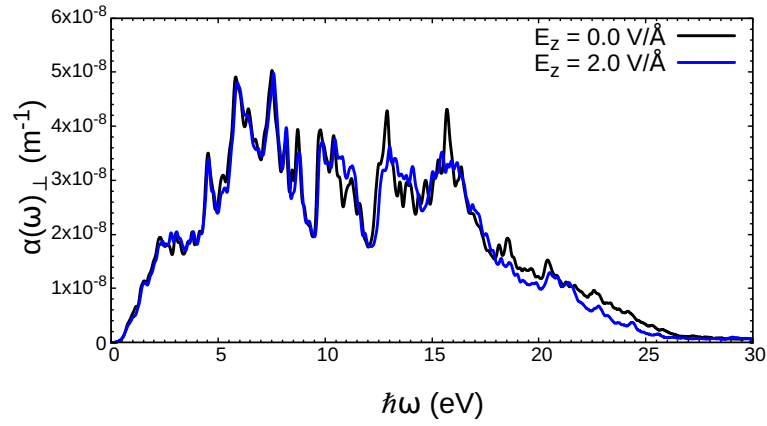
Figure 4.37: For monolayer Mo_2C under $E_z=1.7$ V/Å (a) $\alpha(\omega)_x$ plot. (b) $\alpha(\omega)_y$ plot. (c) $\alpha(\omega)_z$ plot.



(a)

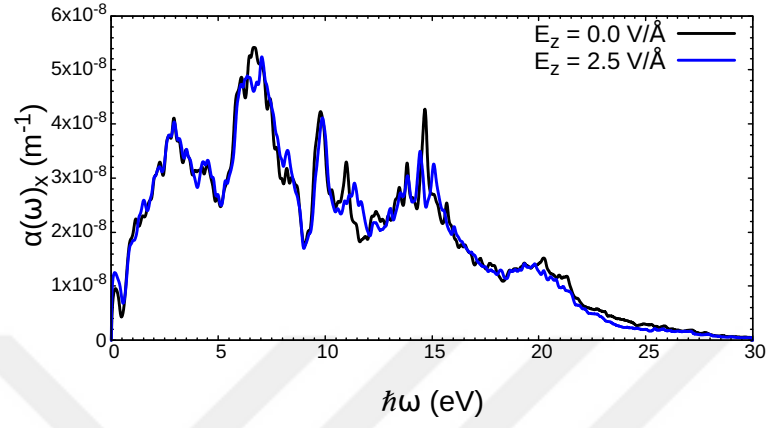


(b)

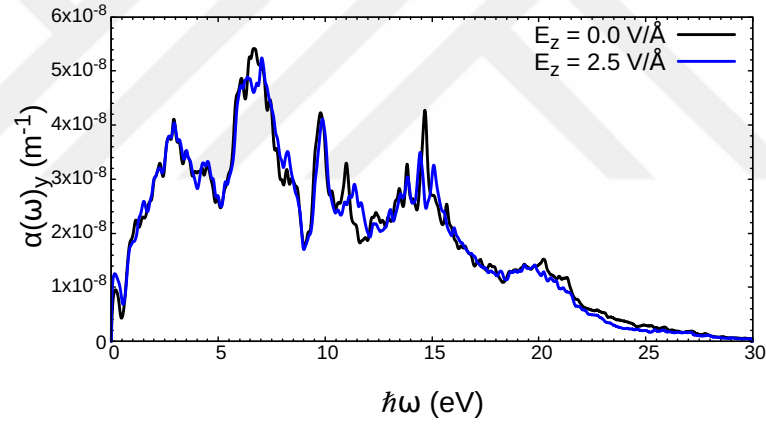


(c)

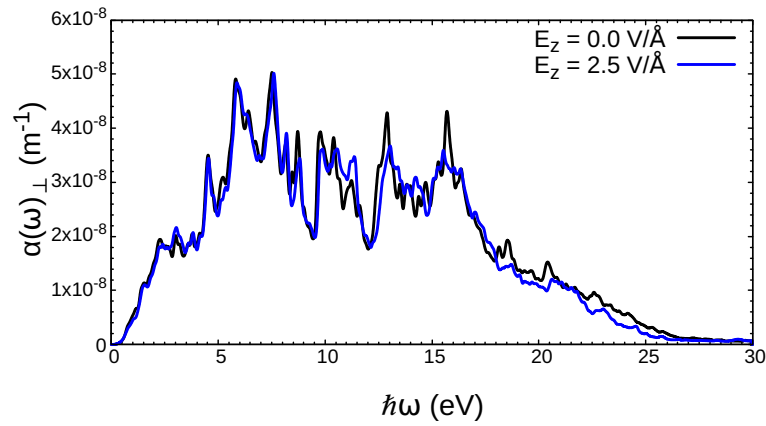
Figure 4.38: For monolayer Mo_2C under the influence of an E-field of strength $E_z=2.0$ V/Å (a) $\alpha(\omega)_x$ plot. (b) $\alpha(\omega)_y$ plot. (c) $\alpha(\omega)_z$ plot.



(a)



(b)



(c)

Figure 4.39: For monolayer Mo_2C in the presence of an E-field of strength $E_z=2.5$ V/Å (a) $\alpha(\omega)_x$ plot. (b) $\alpha(\omega)_y$ plot. (c) $\alpha(\omega)_z$ plot.

Even though intrasmearing contributions are not included for optical calculations, x and y-components of real and imaginary parts of the dielectric function in Fig. 4.15 are in good agreement with those reported in [84] for the case when both intersmearing and intrasmearing contributions were included. However, the vertical component of ε_2 , i.e., components along the z-axis, matched with those when B. Mortazavi et al. considered only intersmearing contribution [84]. In addition to them, our calculations for the absorption coefficient matched with the absorption spectra exhibited in [84]. As concluded in [84], the first main peak in the absorption spectrum around 10 eV is a plasmon peak, corresponding to a π transition. The position of the peak also matched the calculations that Mortazavi et al. performed. By the epsilon.x code, plasmon frequencies are determined as 10.314653414 eV along the x-direction, 10.314639467 eV along the y-direction, and 10.430652200 eV along the z-axis. Therefore, to investigate the effect of E-field on π plasmon transitions, it is a good idea to analyze the position of the peak, i.e., the plasmon frequencies, around 10 eV by increasing E-field strength. In Table 4.1 plasmon frequencies are tabulated. Plasmon frequencies along x, y, and z-directions indicated as PP_x , PP_y , and PP_z , respectively.

E_z (V/Å)	PP_x (eV)	PP_y (eV)	PP_z (eV)
0.0	10.32	10.32	10.43
0.1	10.24	10.24	10.34
0.2	10.20	10.20	10.28
0.3	10.18	10.18	10.24
0.4	10.16	10.16	10.20
0.6	10.16	10.16	10.21
0.8	10.17	10.17	10.22
1.2	10.18	10.18	10.23
1.5	10.19	10.19	10.24
1.7	10.19	10.19	10.24
2.0	10.19	10.19	10.25
2.5	10.20	10.20	10.25

Table 4.1: Plasmon frequencies with changing E-field amplitudes.

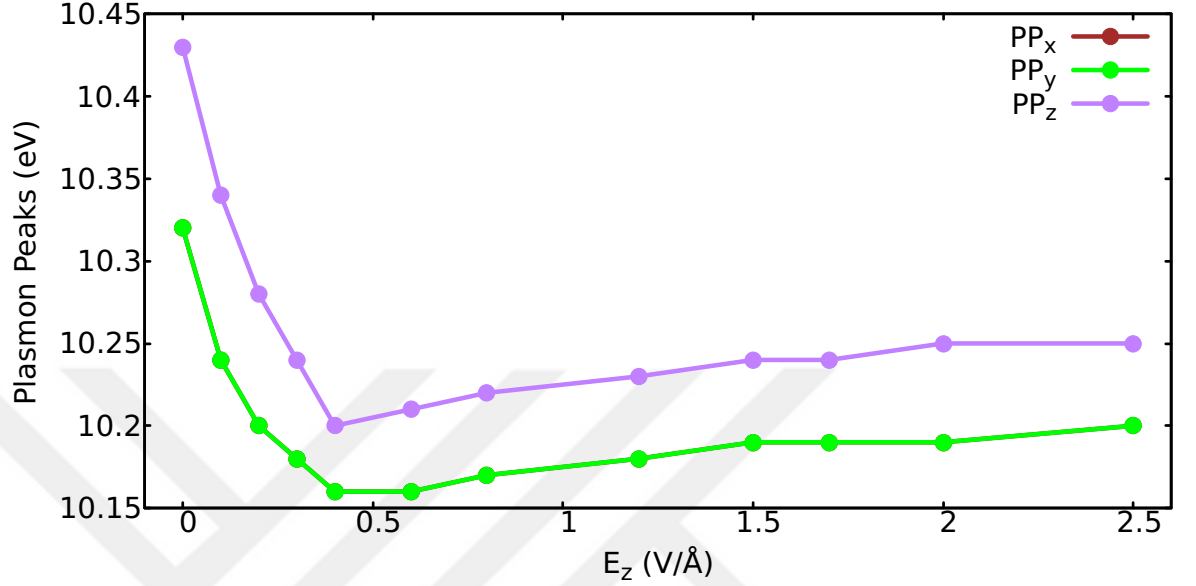


Figure 4.40: Change of PP_x , PP_y , and PP_z under the vertical electric field.

Data corresponding to PP_x and PP_y are the same. Fig. 4.40 is constructed by Table 4.1. Up to 0.4 V/Å , π electron plasmon peaks redshifted whereas after 0.4 V/Å , they blueshifted. Moreover, curves follow almost the same behavior.

To sum up, bands in the VB were degenerate under the vertical electric field and this degeneracy is broken at 0.5 V/Å . Applying a vertical static electric field made n-doping 2D Mo_2C possible after $E_z = 0.8 \text{ V/Å}$ since the s-band that corresponds to the molybdenum atoms shifted below the Fermi level. The corresponding shift and the amount of n-doping got stronger as the E-field increased up to 2.5 V/Å . π electron plasmon peaks redshifted up to 0.4 V/Å whereas those peaks blueshifted for $0.6 \text{ V/Å} \leq E_z \leq 2.5 \text{ V/Å}$.

Chapter 5

Electronic and Optical Properties of Monolayer Tungsten Diselenide under the Perpendicular Static Electric Field

In this chapter, the effects of static E-field applied along the perpendicular direction to the 2D tungsten diselenide (WSe_2) layer are investigated. Structural optimizations, electronic band structure and DOS calculations, and optical properties involving ε_1 and ε_2 are investigated by the ground state calculations from first principles based on DFT. By using QE software all calculations have implemented [65, 66, 67]. Using pw.x code, ground state SCF calculations have been performed whereas optical properties are obtained by epsilon.x code [72]. To investigate the interband transitions between electronic states, calculated optical quantities provide the necessary information. E_z with amplitudes changing between 0.1 V/Å to 2.5 V/Å is applied to the system and all results are compared with those in the absence of the external field.

5.1 Electronic Properties

In all calculations, the convergence threshold for the total energy is determined as 1×10^{-8} Ry. For the structural optimization, the convergence threshold for the forces is taken as 1×10^{-3} Ry, whereas the convergence threshold for stress is determined as 0.5 kbar. By the structural optimization, the distance between nearest-neighboring W and Se atoms is obtained as 2.526 Å, and the lattice constant of 2D WSe_2 system is turned out to be 3.282 Å which is following the experimental values [3, 7]. To prevent possible interactions between the layers, a vacuum of 35.5 Å is introduced to the primitive unit cell of 2D WSe_2 along the z-axis. Since this 2D system is a semiconductor, it has a band gap (E_G). To test the effect of different pseudo-potentials on the values of E_G , two distinct pseudo-potentials are used to describe W and Se atoms while calculating the electronic properties of single-layer WSe_2 : norm-conserving pseudo-potential (NCPP) and projector-augmented-wave pseudo-potential (PAWPP). NCPP is generated by considering the spin-orbit coupling term in the Hamiltonian and is fully relativistic [83]. PAWPP is scalar relativistic and ultrasoft pseudo-potential. For calculating optical properties, only NCPP is utilized to describe W and Se since epsilon.x environment works efficiently with NCPPs. Therefore, except for the comparison of lattice constant and band gap, I will not comment on that much about electronic properties by PAWPP. Band structures agree quite well for both of the pseudo-potentials. XC functional is used as VDW-DF2 to include van der Waals interactions [70]. For the calculations performed using NCPP, for structural optimization and electronic band structure calculations fBZ is sampled on a 20x20x1 Monkhorst-Pack k-mesh [73], whereas for DOS calculations k-mesh sampling was 48x48x1. The kinetic energy cutoff for the plane waves is determined as 240 Ry. Gaussian smearing is utilized during performing SCF calculations. However, for DOS calculations tetrahedron technique is used. For the calculations performed using PAWPP, for structural optimization and electronic band structure calculations k-mesh sampling was 17x17x1, whereas for DOS calculations k-mesh sampling was 48x48x1. The kinetic energy cutoff for the plane waves is determined as 120 Ry. Throughout the SCF calculations, Gaussian smearing is utilized whereas the tetrahedron technique is used for DOS calculations.

This section has two subsections (Section. 5.1.1 and Section. 5.1.2) for electronic calculations with NCPP and PAWPP. After those subsections, another subsection, that is, Ch. 5.1.3 is provided for tuning the band gap and Fermi level of this semiconducting system under E-field. Eventually, optical properties are investigated at the end of this chapter.

5.1.1 Electronic Properties Calculated Using NCPP

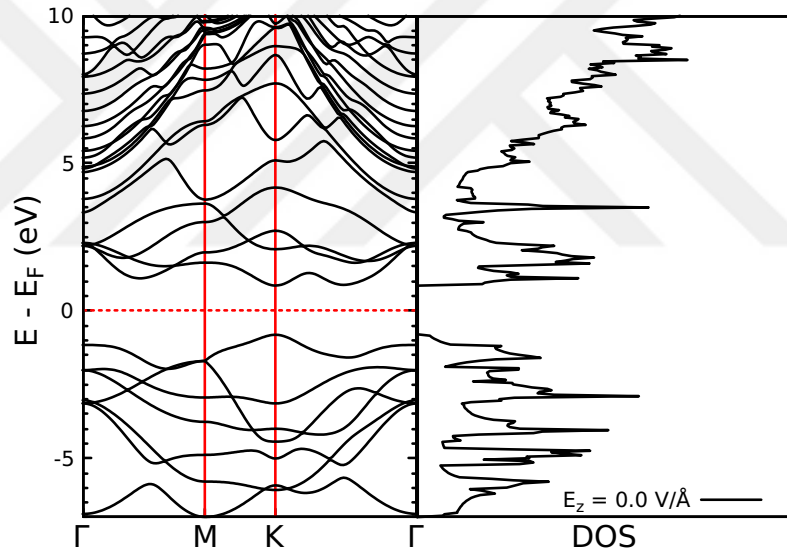


Figure 5.1: Electronic band diagram and DOS of 2D WSe_2 in the absence of external electric field.

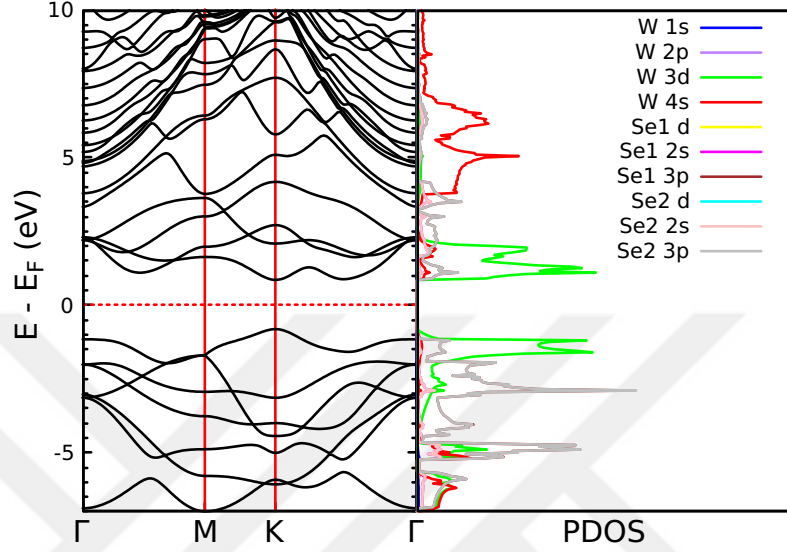


Figure 5.2: Electronic band diagram and projected density of states of 2D WSe_2 in the absence of external electric field.

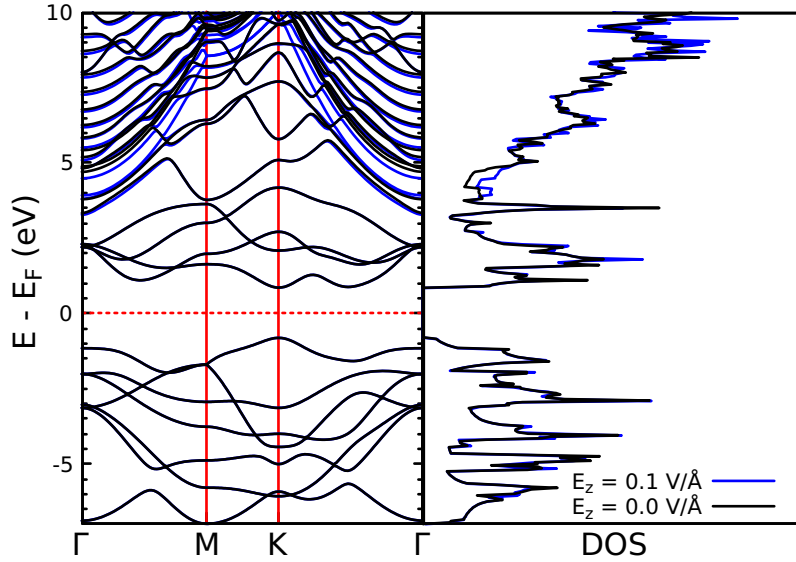


Figure 5.3: Electronic band diagram and DOS of 2D WSe_2 in the presence of an E-field of magnitude $E_z=0.1 \text{ V/\AA}$.

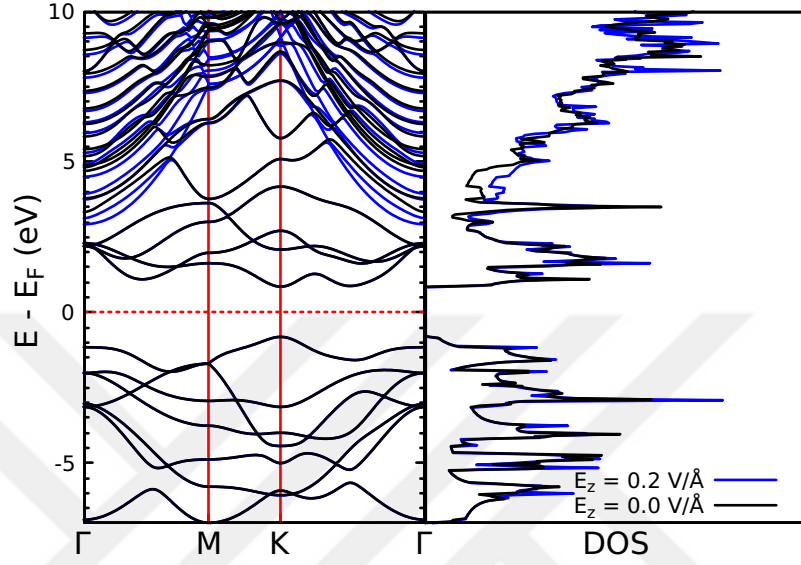


Figure 5.4: Electronic band diagram and DOS of 2D WSe_2 under the influence an external electric field of magnitude $E_z=0.2$ V/Å.

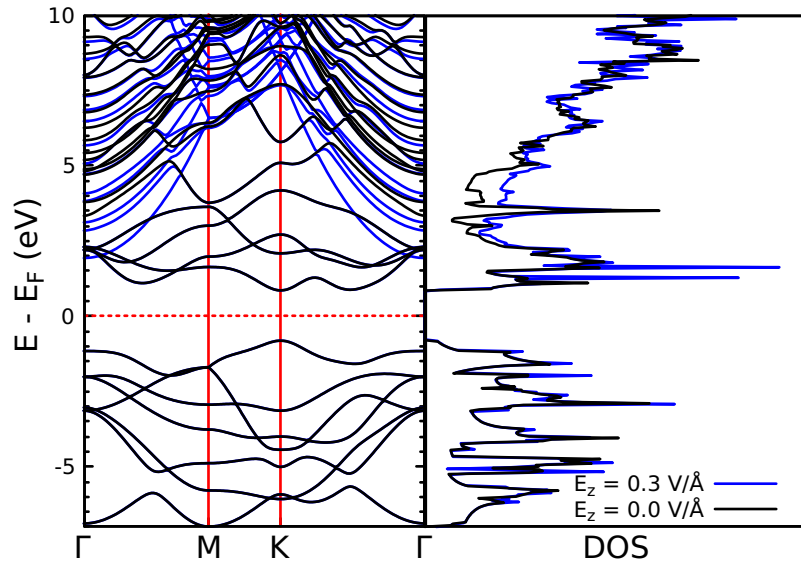


Figure 5.5: Electronic band diagram and DOS of 2D WSe_2 under $E_z=0.3$ V/Å.

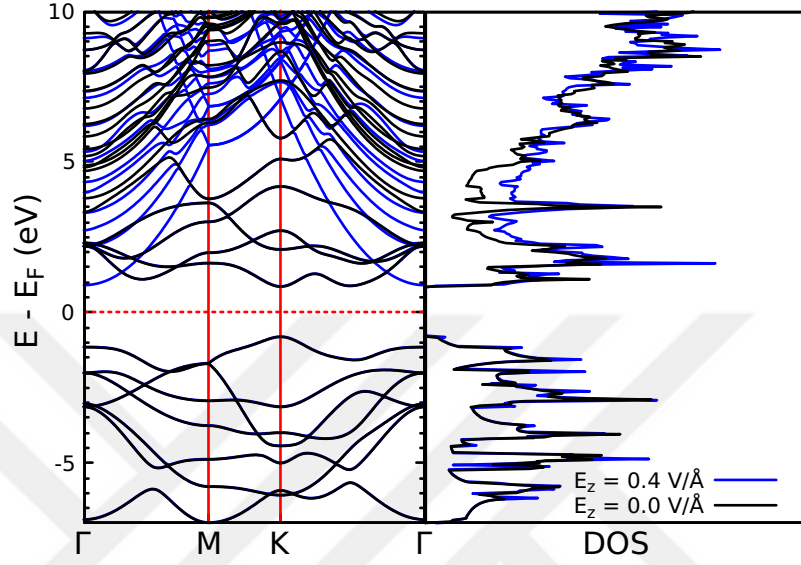


Figure 5.6: Electronic band diagram and DOS of 2D WSe_2 when the perpendicularly applied E-field strength is $E_z=0.4 \text{ V/\AA}$.

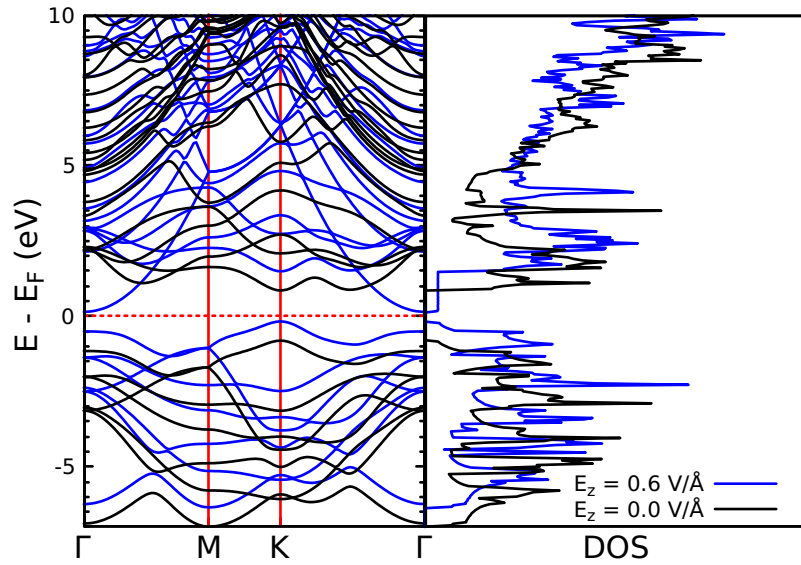


Figure 5.7: Electronic band diagram and DOS of 2D WSe_2 under an E-field of magnitude $E_z=0.6 \text{ V/\AA}$.

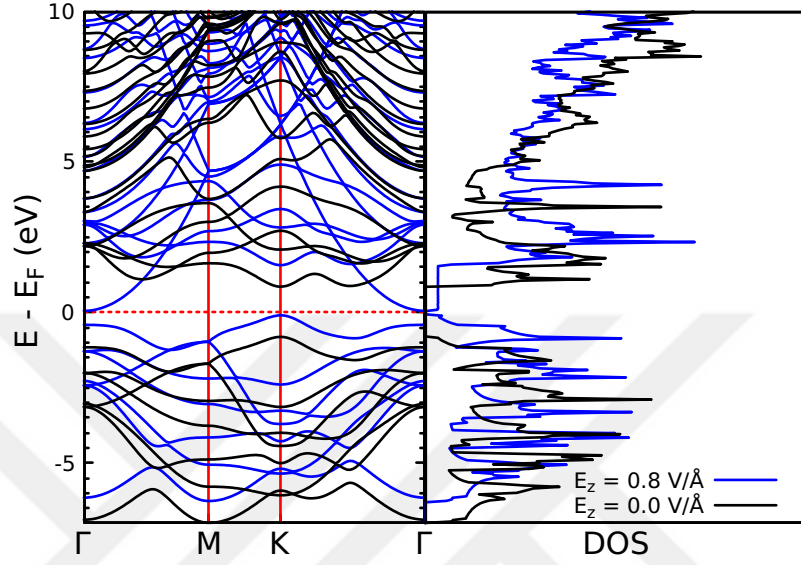


Figure 5.8: Electronic band diagram and DOS of 2D WSe_2 when the perpendicularly applied E-field $E_z=0.8$ V/Å.

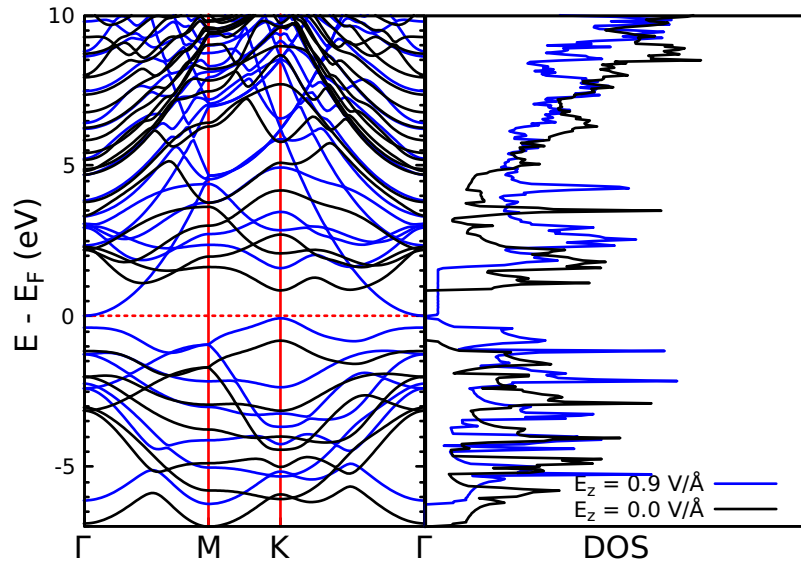


Figure 5.9: Electronic band diagram and DOS of 2D WSe_2 in the presence of an electric field of magnitude $E_z=0.9$ V/Å.

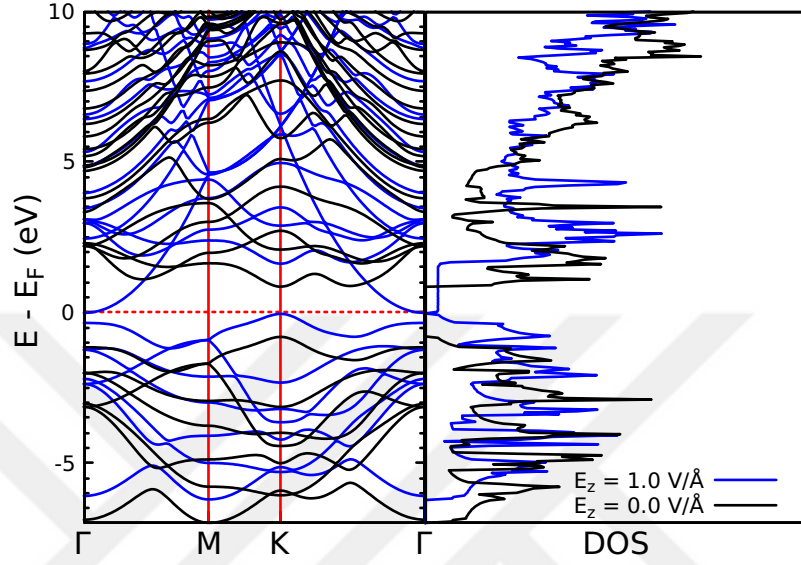


Figure 5.10: Electronic band diagram and DOS of 2D WSe_2 in the presence of an electric field of magnitude $E_z=1.0 \text{ V/\AA}$.

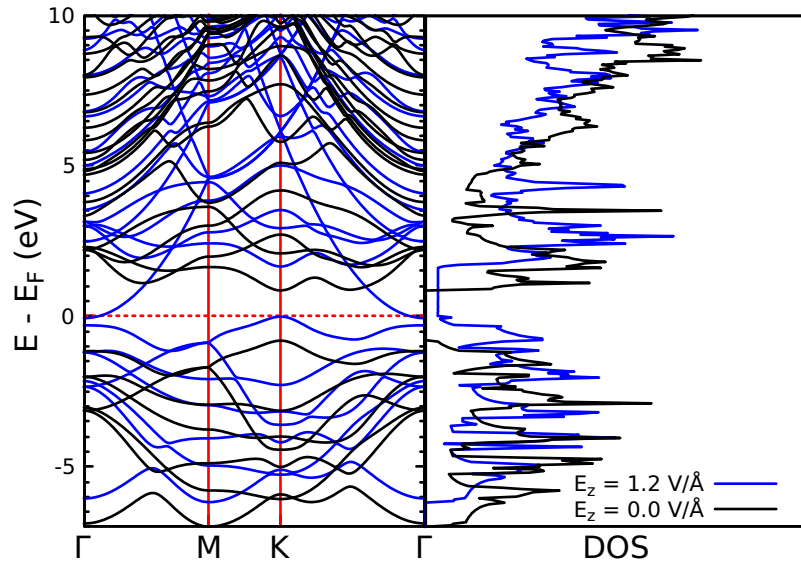


Figure 5.11: Electronic band diagram and DOS of 2D WSe_2 under the influence of an external electric field of magnitude $E_z=1.2 \text{ V/\AA}$.

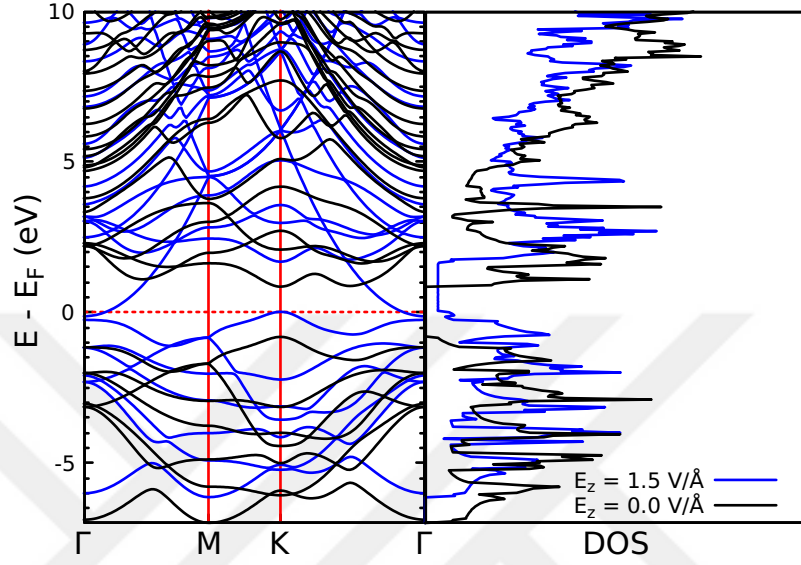


Figure 5.12: Electronic band diagram and DOS of 2D WSe_2 under $E_z=1.5 \text{ V/\AA}$.

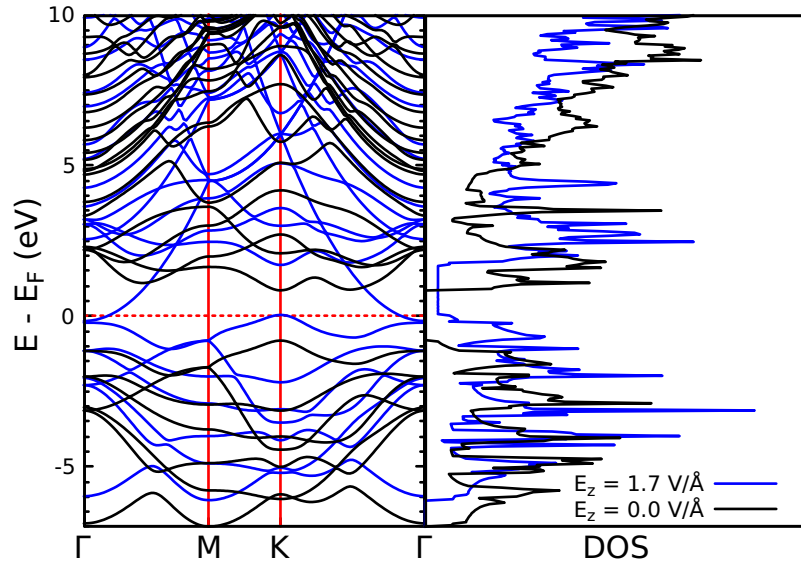


Figure 5.13: Electronic band diagram and DOS of 2D WSe_2 under an external electric field of magnitude $E_z=1.7 \text{ V/\AA}$.

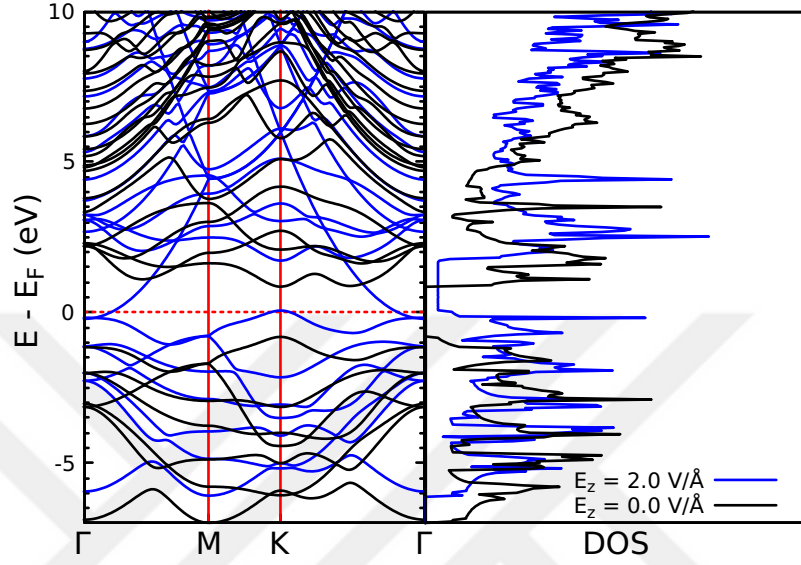


Figure 5.14: Electronic band diagram and DOS of 2D WSe_2 in the presence of an external electric field of magnitude $E_z=2.0 \text{ V/\AA}$.

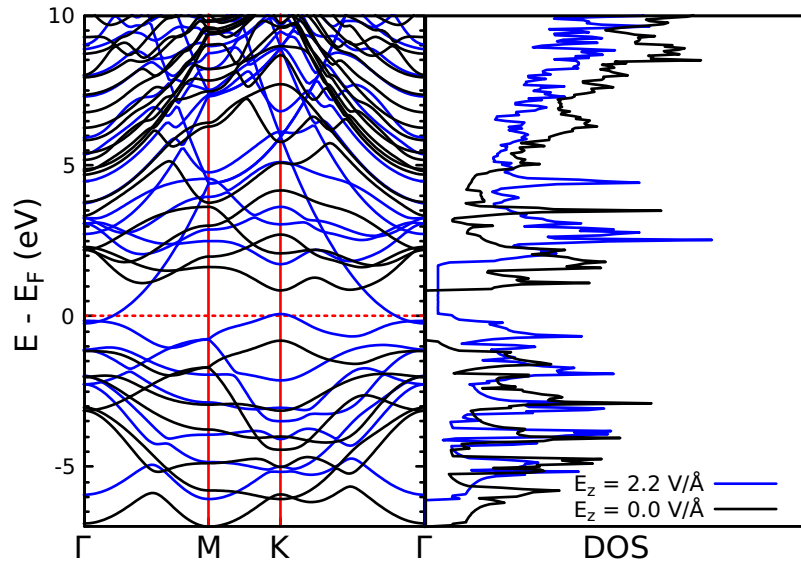


Figure 5.15: Electronic band diagram and DOS of 2D WSe_2 under $E_z=2.2 \text{ V/\AA}$.

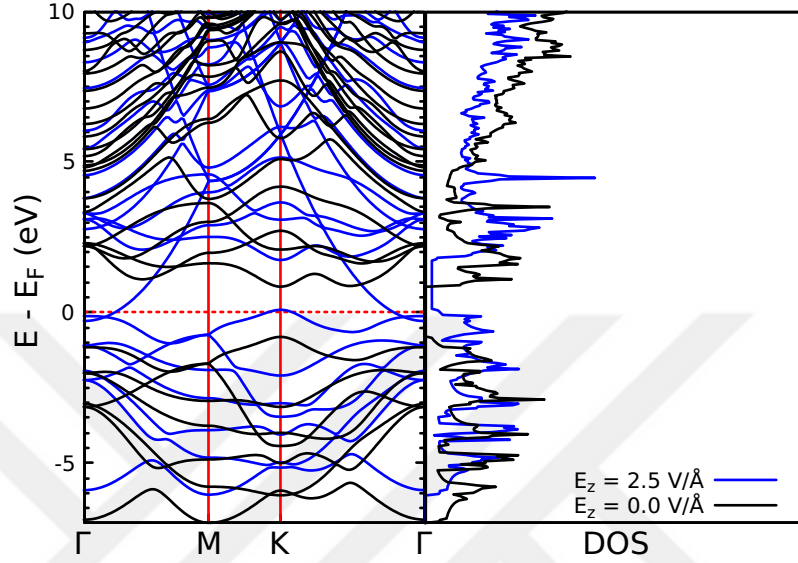


Figure 5.16: Electronic band diagram and DOS of 2D WSe_2 in the presence of an external electric field of magnitude $E_z=2.5$ V/Å.

In Fig. 5.1 electronic band diagram and DOS of 2D WSe_2 is obtained whereas electronic band structure data together with PDOS is provided in 5.2. In the PDOS plot, W 3d means d-orbital corresponding to the tungsten atom and it is the third wave function component. Se2 2s describes that it is the second Se atom in single-layer tungsten diselenide system, the corresponding orbital is s-orbital and it is the second wave function component, and so on. As can be seen with ease by PDOS, VBM, and CBM are dominated by the electrons of the d-orbital of the W atom in the majority. Moreover, p-orbitals of Se atoms contribute to VBM and CBM, as well. Above 3.5 eV is dominated by the s-orbitals of W whereas below -1 eV is dominated by the p-orbitals of Se.

For $0.0 \text{ V/Å} \leq E_z \leq 0.4 \text{ V/Å}$, no significant shift is observed in the VB, i.e., VB is degenerate between 0.0 V/Å and 0.4 V/Å . However, as we introduced the E-field, the most obvious shifts in the CB are the shifts corresponding to the bands of W-s (s-orbital of W atom) that are shifted in the direction towards E_F , i.e., they shifted downwards.

At $E_z = 0.1 \text{ V/\AA}$, the band slightly below 3.5 eV barely shifted, that is the band corresponding to Se-p (p-orbital of Se atoms) and the downwards shifts due to W-s and Se-p became greater by increasing E-field. Moreover, starting from $0.1 \text{ V/\AA}$, shifts around 10 eV (higher energy region in the CB) became stronger as the amplitude of the E-field increased.

Starting from $E_z = 0.6 \text{ V/\AA}$, degeneracy in the VB is broken and strong shifts started to occur towards the Fermi level, i.e., upward shifts came into account. At $E_z = 0.6 \text{ V/\AA}$, the band corresponding to the d-orbital of W got closer to the Fermi level and shifted about 0.5 eV upwards from its position where there was no-E-field. Similar to the W-d, bands corresponding to the p orbitals of Se atoms and those corresponding to the s-orbitals of W shifted upwards as well in the VB and they continued shifting in the upwards direction with increasing E-field strengths.

After $0.8 \text{ V/\AA}$, the band due to W-s started to touch the Fermi level, and the band gap became quite low. At $1.0 \text{ V/\AA}$, the band gap disappeared and a semiconductor-to-metal transition occurred in that system. Moreover, the band due to W-s got lower with increasing strengths of the electric field that enabled us to dope 2D tungsten diselenide under the vertical electric field. Similar to the previously investigated 2D systems, vertical static electric field is used to n-dope monolayers. Changes in band gap and Fermi energy with increasing amplitudes of the static vertical electric field are tabulated, plotted and mentioned in Chapter 5.1.3.

As the E-field strength increased, bands between 2.0 eV and 2.5 eV (bands corresponding to W-d and Se-p) shifted upwards starting from $E_z = 0.6 \text{ V/\AA}$ and the shift became stronger with increasing E-field amplitude. In the no-E-case last mentioned four bands merged at the same level at Γ point in the fBZ. However, this circumstance did not last that long after $0.6 \text{ V/\AA}$ and they separated from the point at Γ and the amount of separation increased more under stronger E-field amplitudes. The broken degeneracy in the VB can be relatable with the transition that took place around $0.6 \text{ V/\AA}$ in Fig. 5.33.

5.1.2 Electronic Properties Calculated Using PAWPP

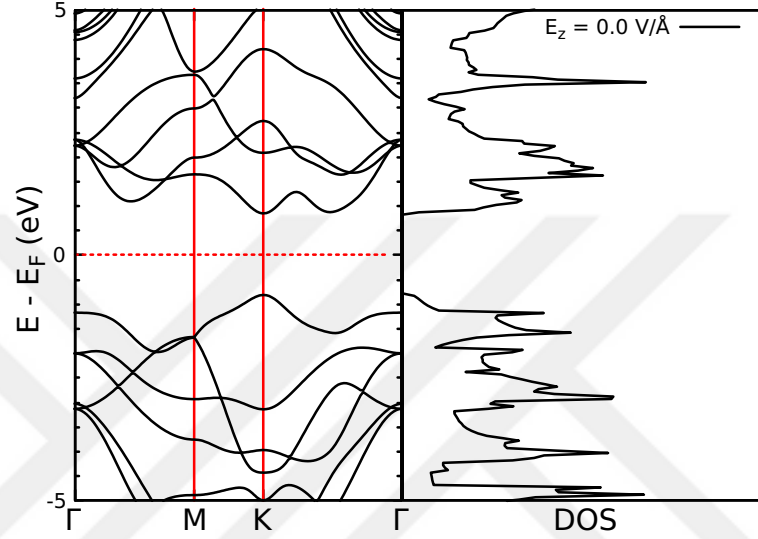


Figure 5.17: Electronic band diagram and DOS of 2D WSe_2 in the absence of external electric field.

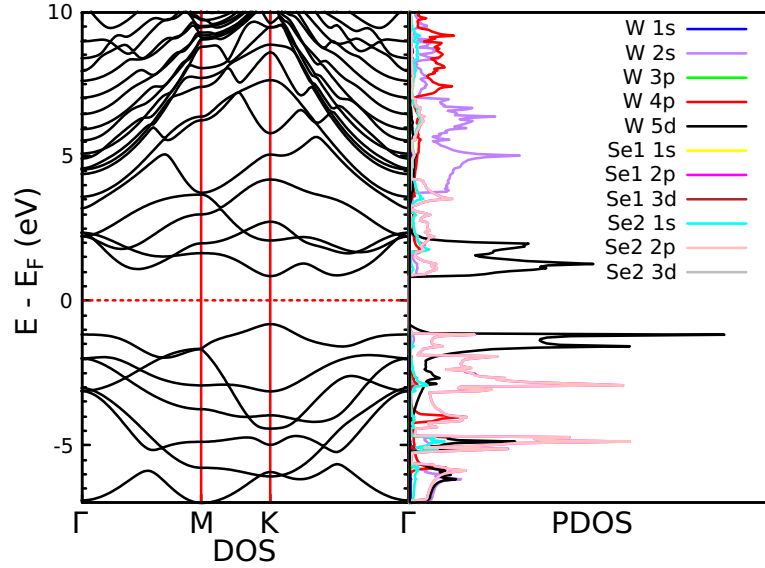


Figure 5.18: Electronic band diagram and projected density of states of 2D WSe_2 in the absence of external electric field.

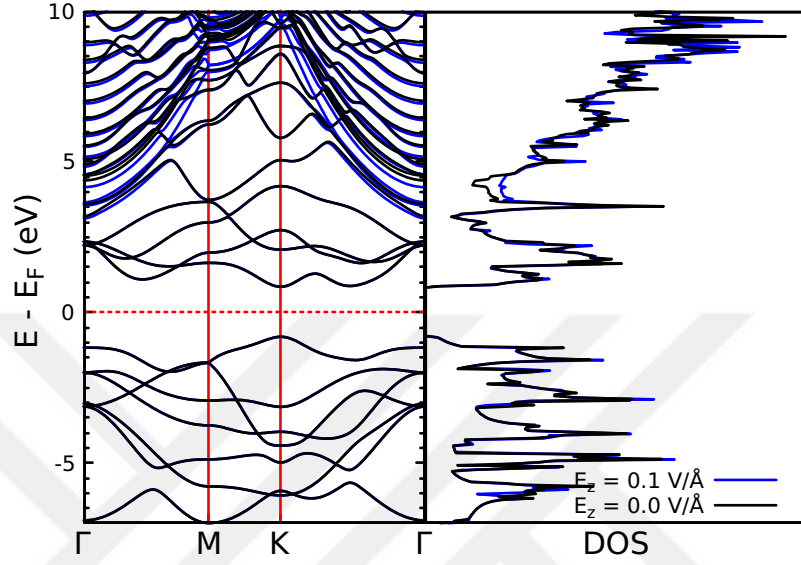


Figure 5.19: Electronic band diagram and DOS of 2D WSe_2 in the presence of an external electric field of magnitude $E_z=0.1 \text{ V/\AA}$.

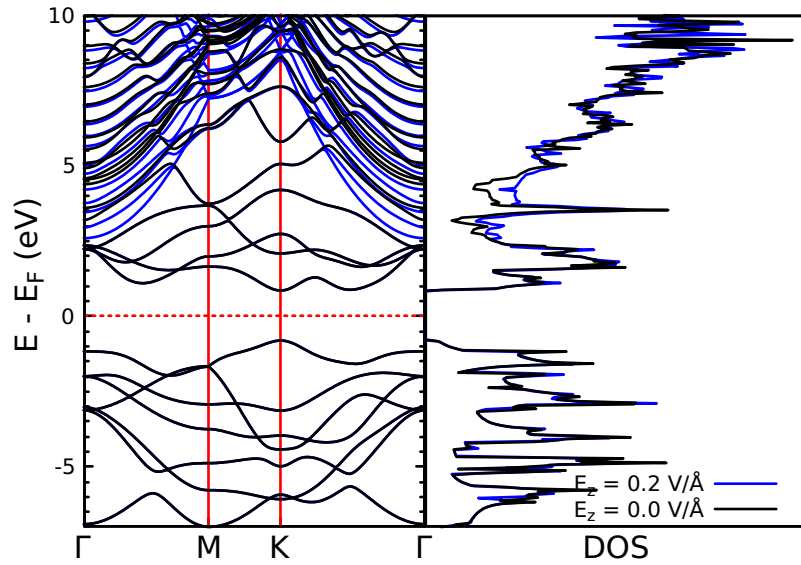


Figure 5.20: Electronic band diagram and DOS of 2D WSe_2 when the magnitude of the E-field is $E_z=0.2 \text{ V/\AA}$.

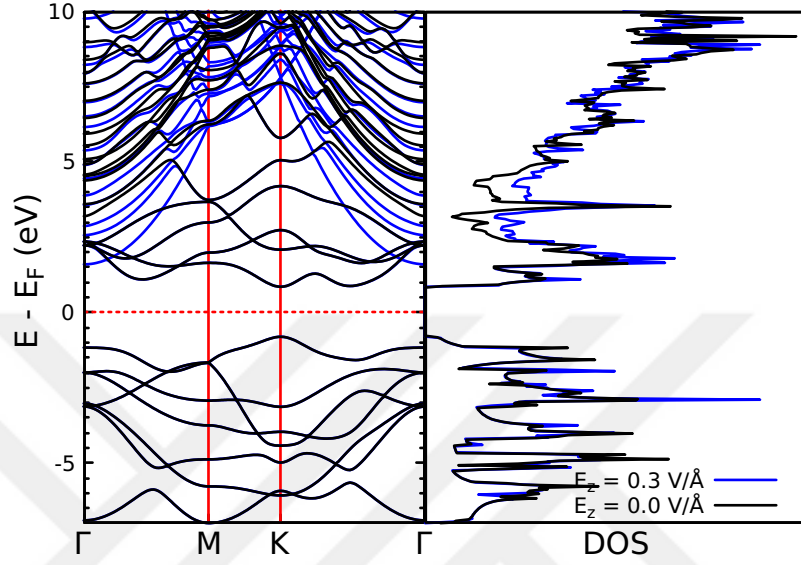


Figure 5.21: Electronic band diagram and DOS of 2D WSe_2 under an E-field of magnitude $E_z=0.3 \text{ V/\AA}$.

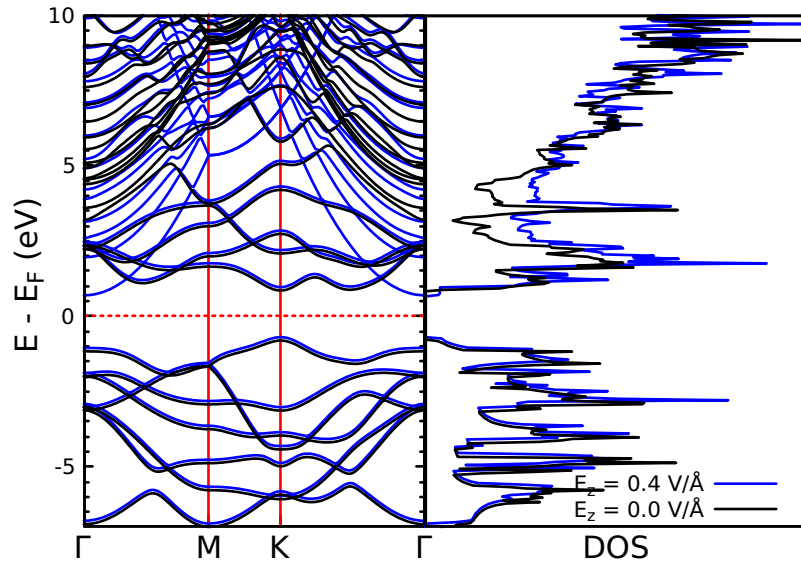


Figure 5.22: Electronic band diagram and DOS of 2D WSe_2 under $E_z=0.4 \text{ V/\AA}$.

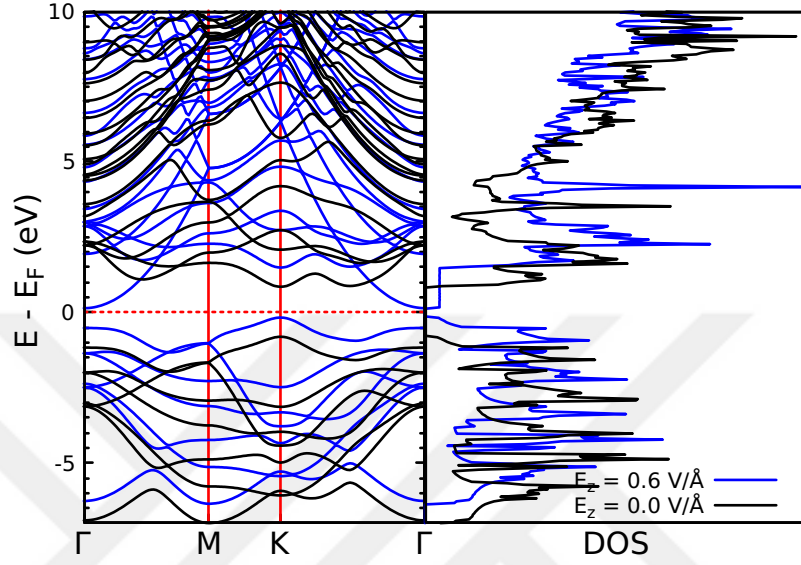


Figure 5.23: Electronic band diagram and DOS of 2D WSe_2 under the influence of an E-field strength of $E_z=0.6$ V/Å.

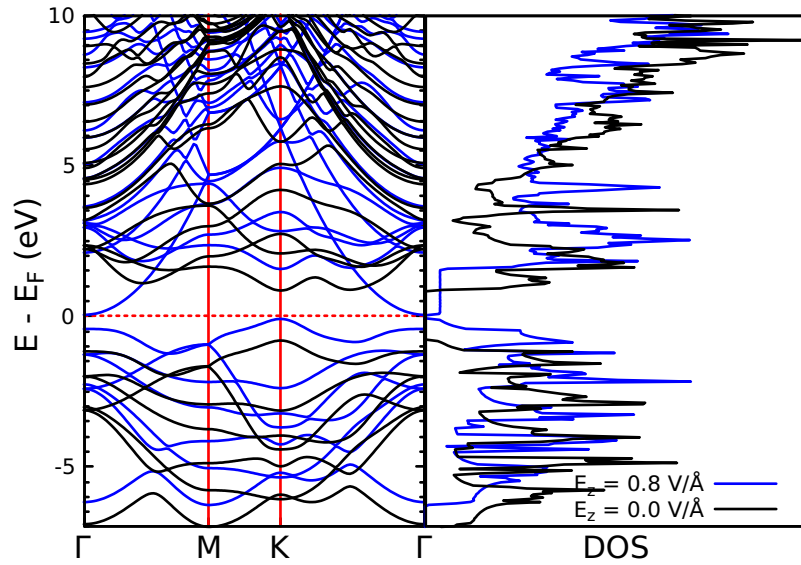


Figure 5.24: Electronic band diagram and DOS of 2D WSe_2 in the presence of an E-field of magnitude $E_z=0.8$ V/Å.

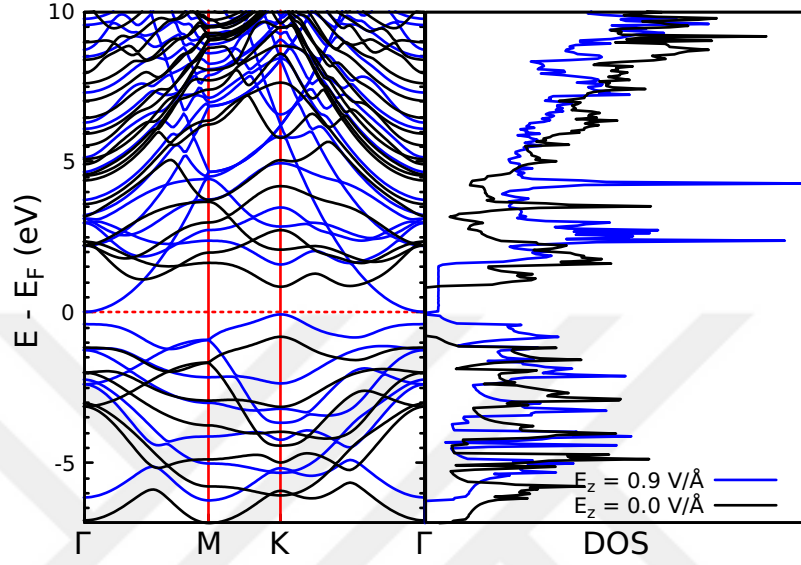


Figure 5.25: Electronic band diagram and DOS of 2D WSe_2 under $E_z=0.9 \text{ V/\AA}$.

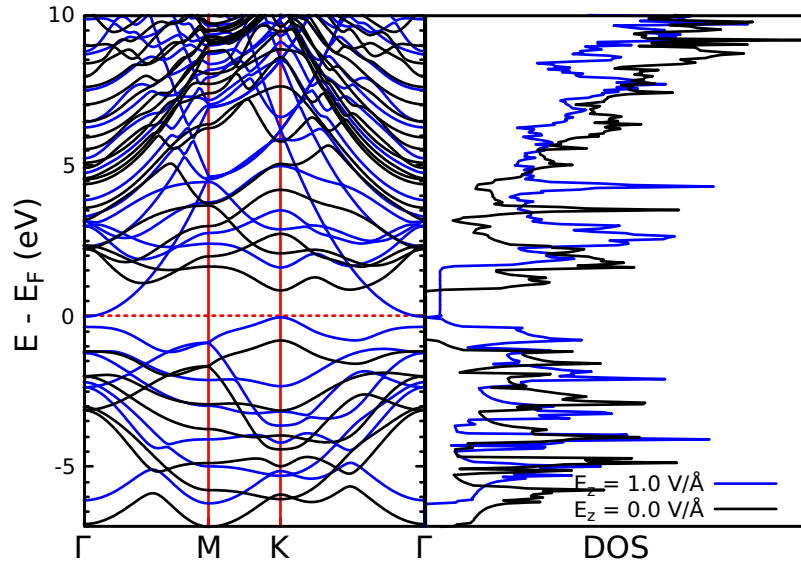


Figure 5.26: Electronic band diagram and DOS of 2D WSe_2 under an E-field of magnitude $E_z= 1.0 \text{ V/\AA}$.

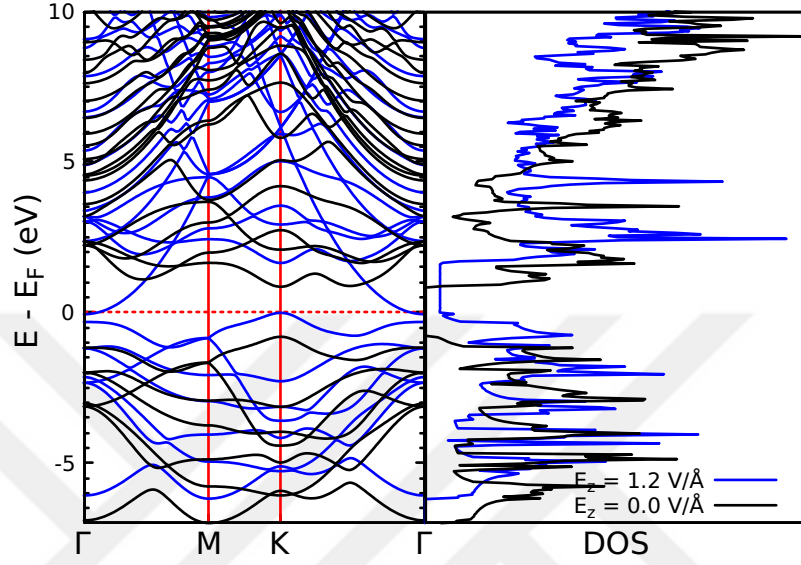


Figure 5.27: Electronic band diagram and DOS of 2D WSe_2 in the presence of an E-field of magnitude $E_z = 1.2 \text{ V/\AA}$.

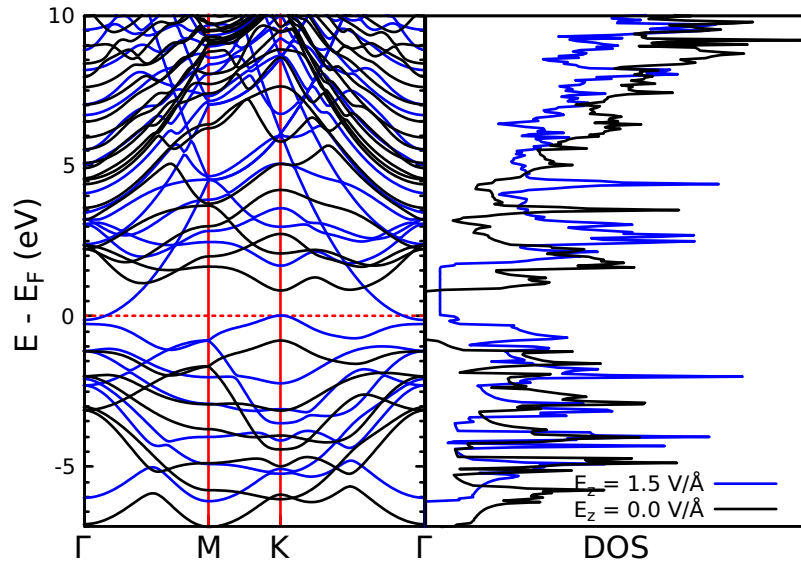


Figure 5.28: Electronic band diagram and DOS of 2D WSe_2 when the strength of perpendicularly applied E-field is $E_z = 1.5 \text{ V/\AA}$.

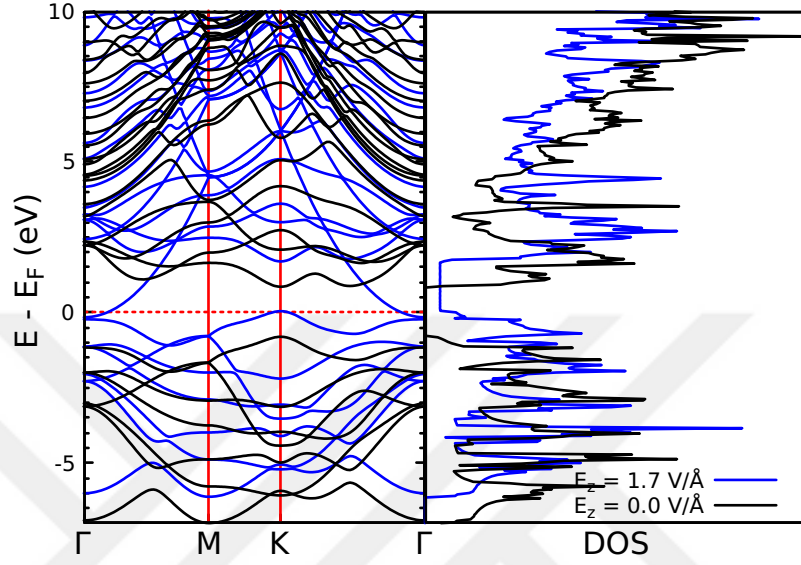


Figure 5.29: Electronic band diagram and DOS of 2D WSe_2 under $E_z = 1.7$ V/Å.

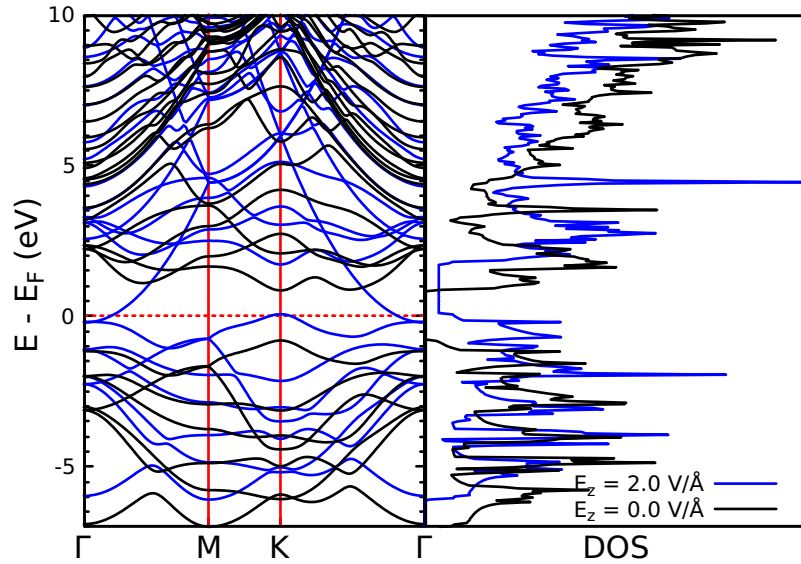


Figure 5.30: Electronic band diagram and DOS of 2D WSe_2 in the presence of an E-field of magnitude $E_z = 2.0$ V/Å.

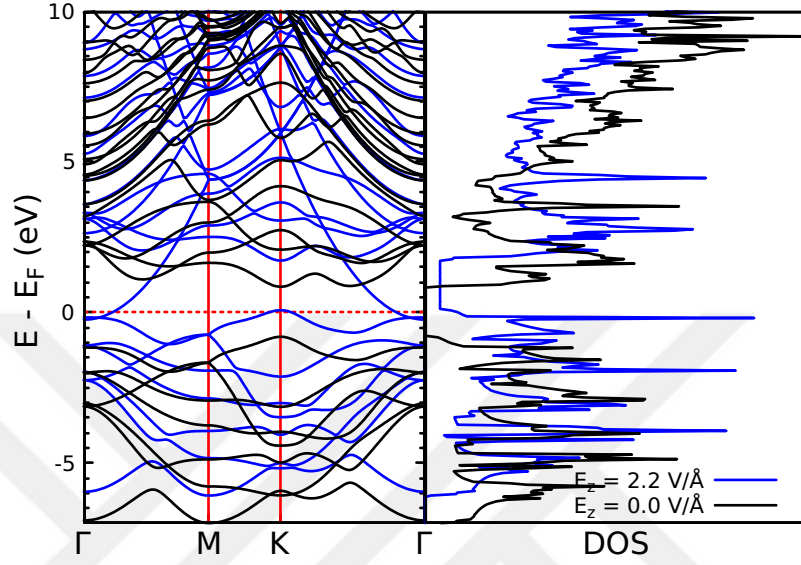


Figure 5.31: Electronic band diagram and DOS of 2D WSe_2 under the influence of an E-field magnitude of $E_z = 2.2 \text{ V/\AA}$.

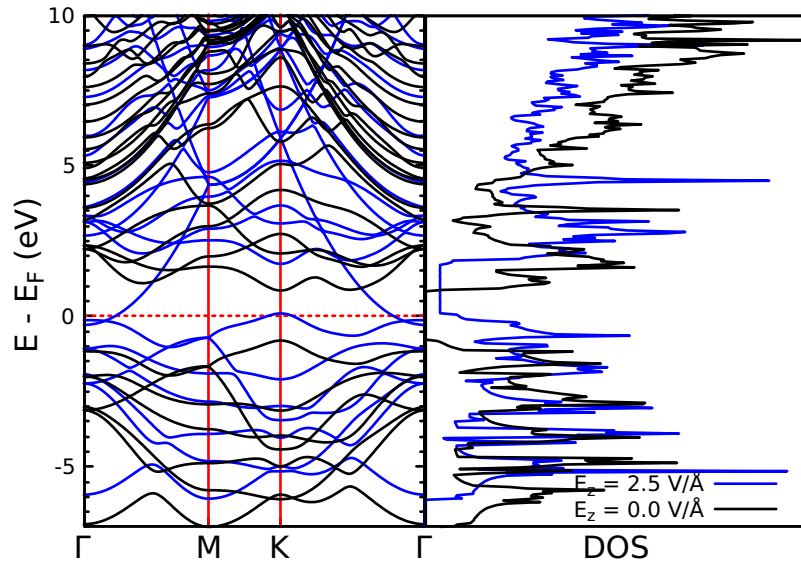


Figure 5.32: Electronic band diagram and DOS of 2D WSe_2 in the presence of an E-field of magnitude $E_z = 2.5 \text{ V/\AA}$.

In Fig. 5.17 electronic band diagram and DOS of 2D WSe_2 by PAWPP is obtained whereas electronic band structure data together with PDOS is provided in Fig. 5.18. By PDOS, VBM and CBM are dominated by d-orbitals of W atom in majority. Additionally, p-orbitals of Se atoms contribute to VBM and CBM, as well. Around 4 eV, s-orbital contribution coming from W is present and above 6.5 eV p-orbitals of tungsten atom are in majority. In general, the energy region below -1 eV is dominated by s-orbitals of Se. The same shifts are observed in electronic band structures under the vertical E-field as commented on the NCPP case. As observed in Chapter 5.1.1, after 0.8 V/Å, the band corresponding to the s-orbital of the tungsten atom got closer to the Fermi level, and the band gap decreased drastically. When $E_z = 1.0$ V/Å, E_G became zero and a semiconductor-to-metal transition is observed. Additionally, the band due to W-s got lower as the E-field increased which makes it possible to n-dope monolayer WSe_2 under the vertical electric field. Starting from $E_z = 0.6$ V/Å, by increasing E-field amplitudes, bands corresponding to W-d and Se-p shifted upwards. In the absence of any external fields, the last cited bands merged at the same level at Γ point in the fBZ. However, those bands separated from the point at Γ and the separation became stronger by increasing amplitudes of the E-field.

5.1.3 Tuning E_G and E_F under E_z

As mentioned previously, applying external factors such as electric field or strain may change material properties. For this semiconducting system, a static electric field in the interval of $0.1 \text{ V/Å} \leq E_z \leq 2.5 \text{ V/Å}$ is applied perpendicular to the layer of tungsten diselenide, i.e., along the +z-axis as have applied throughout this thesis, and that external effect changed the electronic properties drastically. In Chapter 1, a literature overview was provided, and is stated that applying electric field may change the band gap and position of Fermi level of materials. In the absence of any external effects, it is found that single-layer tungsten diselenide has a band gap of 1.649 eV (1.600 eV) when NCPP (PAWPP) is used in the calculations.

Quantity	Thesis Results	Literature Results
E_G (eV)	$1.60^P, 1.65^N$	$1.75^a, 1.25^b,$ $1.63^b, 1.62^e,$ $1.19^f, 1.68^f$
a (Å)	$3.282^P, 3.282^N$	$3.623^a, 3.519^a,$ $3.320^b, 3.29^b,$ $3.286^c, 3.247^d,$ $3.316^d, 3.323^d,$ $3.290^e, 3.32^f,$ 3.28^g

Table 5.1: Lattice constant (a) and value of direct band gap results obtained in this thesis (Thesis Results column) and those in the literature (Literature Results column). ^{P} stands for PAWPP calculations, ^{N} represents NCPP calculations. Following letters correspond to the results in the literature: ^{a} [1], ^{b} [2], ^{c} [3], ^{d} [4], ^{e} [5], ^{f} [6], ^{g} [7].

In Table 5.1, results for the lattice constant (a) and value of direct band gap obtained in this thesis and results in the literature have been reported for comparison. XC functional used in the thesis is VDW-DF2 [70]. I group results in the literature by the utilized XC functional. They mainly used Perdew-Burke-Ernzerhof (PBE) [85], Heyd-Scuseria-Ernzerhof (HSE) [86], and Grimme-d2 method (to include van der Waals effects). The lattice constant is calculated as $a = 3.519$ Å by Grimme-d2, and $a = 3.623$ Å by PBE in [1]. The band gap is calculated as $E_G = 1.19$ eV by PBE in [6] and $E_G = 1.68$ eV by HSE in [2]. In general, PBE underestimates the band gap when the van der Waals interactions are significant for the materials [1, 2]. However hybrid functionals such as HSE or functionals considering van der Waals interactions such as VDW-DF2 are in good agreement with their actual results. As indicated, thesis results for E_G are 1.60 eV and 1.65 eV which agree with [2] (HSE case), [5], and [6]. The lattice constants are the same for NCPP and PAW cases and my results for a are also in good agreement with the experimental lattice constant values which are 3.286 Å [3] and 3.28 Å [7]. Deviations in the cited quantities between articles are due to utilized XC functionals, and different kinds of pseudo-potentials since the electronic charge densities are calculated differently.

Table 5.2 (Table 5.3) contains the change in band gap of 2D WSe_2 when the utilized pseudo-potential is NCPP (PAWPP). For both utilized pseudo-potentials, E_G decreased as the strength of the external field increased, and E_G disappeared (became zero) for $E_z \geq 1.0$ V/Å which is quite interesting but expected since E-field can significantly tune material properties.

E_z (V/Å)	E_G (eV)
0.0	1.65
0.1	1.65
0.2	1.60
0.3	1.60
0.4	1.59
0.6	0.29
0.8	0.10
0.9	0.05
1.0	0.00

Table 5.2: Change of band gap with increasing E-field strengths for calculations performed by using NCPP.

A semiconductor-to-metal transition is observed when $E_z \geq 1.0$ V/Å. Data in Tables 5.2 and 5.3 are visualized in Fig. 5.33. In E_G , a significant decrease is observed when $E_z \geq 0.4$ V/Å for both of the pseudo-potentials. From the first principles, Nguyen et al. observed a similar transition that took place for one of the TMDs, 2D MoS_2 with a plot similar to the one in Fig. 5.33 [87].

E_z (V/Å)	E_G (eV)
0.0	1.60
0.1	1.59
0.2	1.59
0.3	1.65
0.4	1.35
0.6	0.25
0.8	0.10
0.9	0.08
1.0	0.00

Table 5.3: Change of band gap with increasing E-field strengths for calculations performed by using PAWPP.

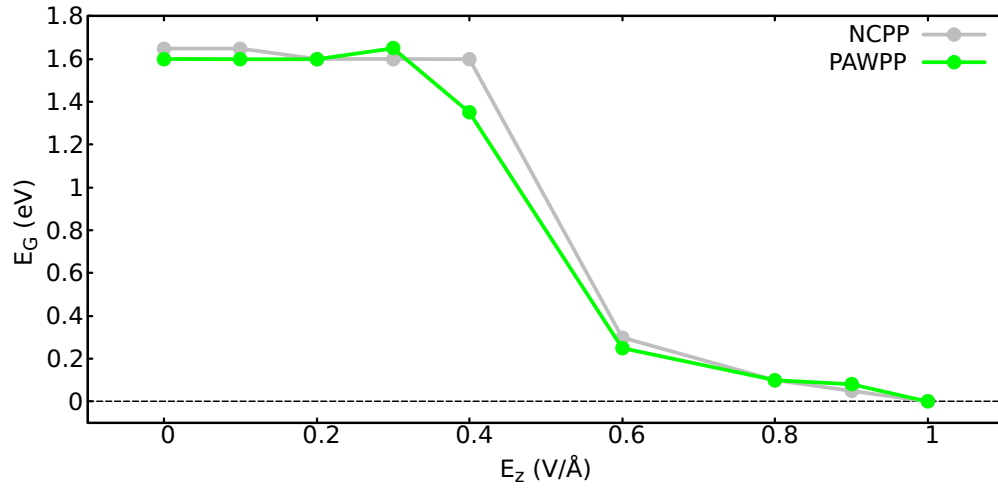
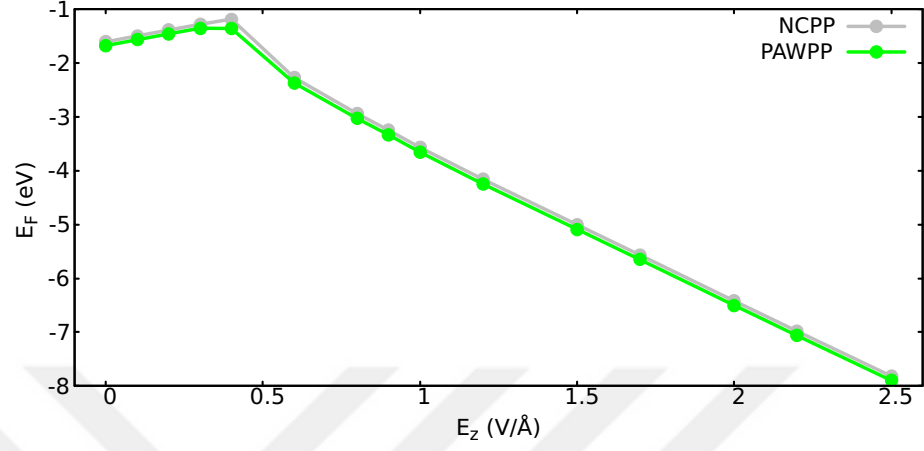
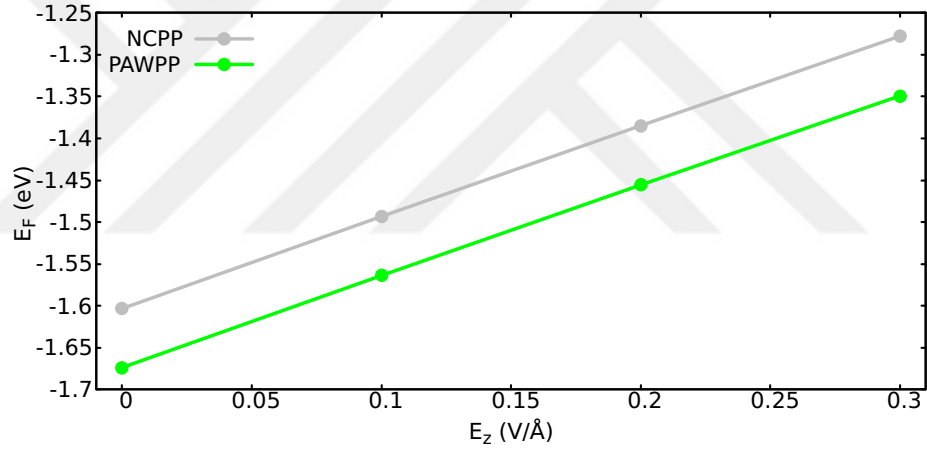


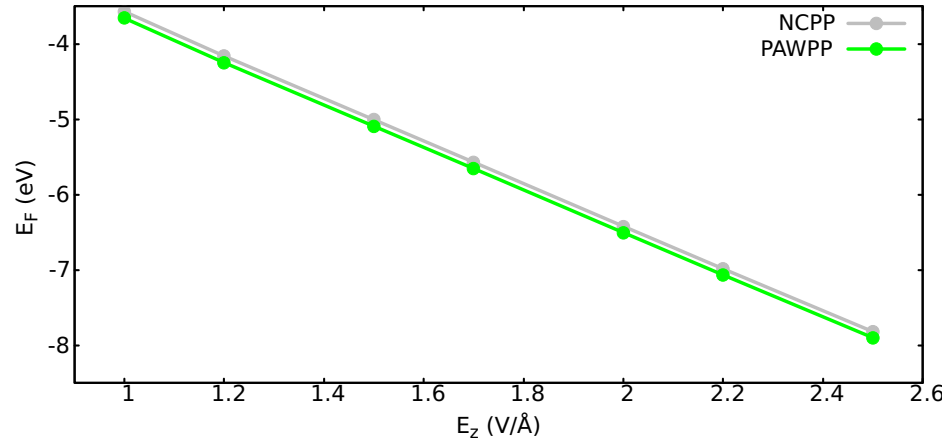
Figure 5.33: Change of band gap of 2D WSe_2 with respect to the external electric field for calculations performed by utilizing NCPP and PAWPP.



(a)



(b)



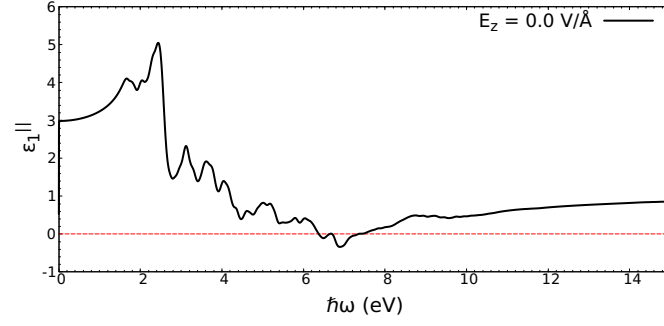
(c)

Figure 5.34: Change in E_F due to distinct values of amplitudes corresponding to the applied electric field for calculations performed by making use of NCPP and PAWPP. (a) $0.0 \text{ V/Å} \leq E_z \leq 2.5 \text{ V/Å}$. (b) $0.0 \text{ V/Å} \leq E_z \leq 0.3 \text{ V/Å}$. (c) $1.0 \text{ V/Å} \leq E_z \leq 2.5 \text{ V/Å}$.

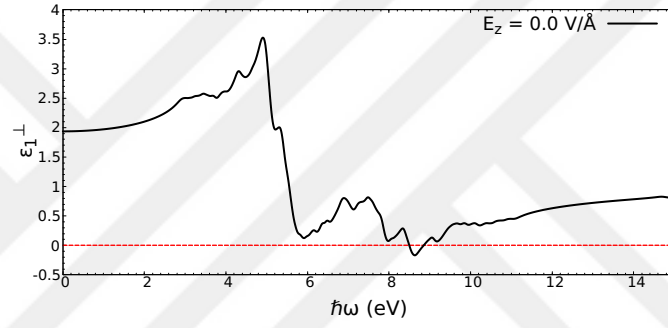
As we have done for monolayer graphene and 2H molybdenum carbide, change in E_F under the vertical electric field for the current system is examined by the SCF calculations and illustrated in Fig. 5.34. In addition to those, since we considered two different pseudo-potentials -NCPP and PAWPP- while investigating the electronic properties, change in E_F in the presence of E-field is plotted for two of them. In general, the behavior of E_F obtained by using NCPP and PAWPP coincided and they agreed with each other. When the amplitude of the E-field is between $0.0 \text{ V/\AA}$ and $0.3 \text{ V/\AA}$, there is a linear increase in E_F . However, a linear decrease is observed for $1.0 \text{ V/\AA} \leq E_z \leq 2.5 \text{ V/\AA}$ as we observed in preceding 2D systems. Apparently, E_F started to decrease when $E_z = 0.4 \text{ V/\AA}$ and preserved this circumstance up to $2.5 \text{ V/\AA}$.

5.2 Optical Properties

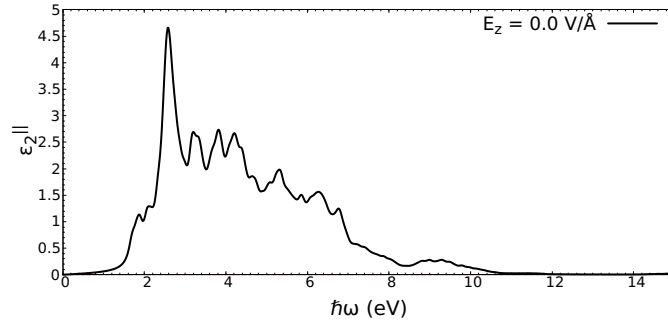
For the optical calculations epsilon.x code is implemented and k-points are used with equal weights with a uniform grid by writing coordinates and equal weights manually. SCF calculations for optical properties are also repeated with equal weighted k-points. Number of manually written coordinates are taken as 841 corresponding to a $29 \times 29 \times 1$ k-mesh sampling. Gaussian smearing is used for SCF and optical calculations. The same method is used as utilized in Chapters 3.2 and 4.2, therefore, the same theory applies for 2D tungsten diselenide as well. Perpendicular and horizontal components of real and imaginary parts of the dielectric function have been plotted. Horizontal components of $\epsilon_1(\omega)$ and $\epsilon_2(\omega)$ are calculated by Eq. 3.10 and Eq. 3.11. In the absence of E-field, horizontal and perpendicular components of real and imaginary parts of dielectric function have shown in Fig. 5.35. Notice that excitonic transitions are not considered since they are beyond this thesis.



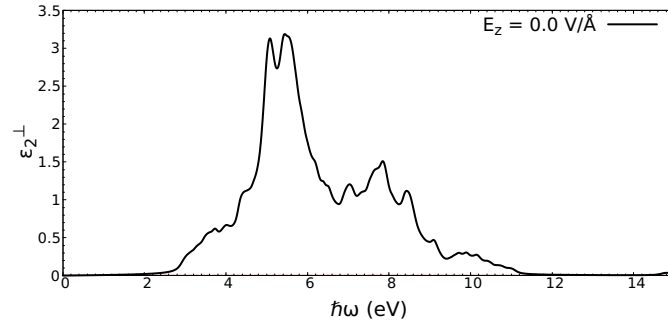
(a)



(b)

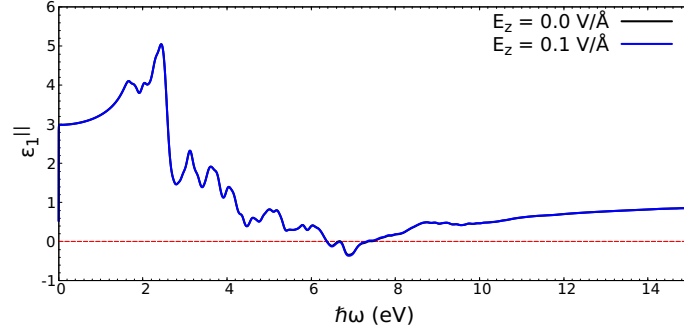


(c)

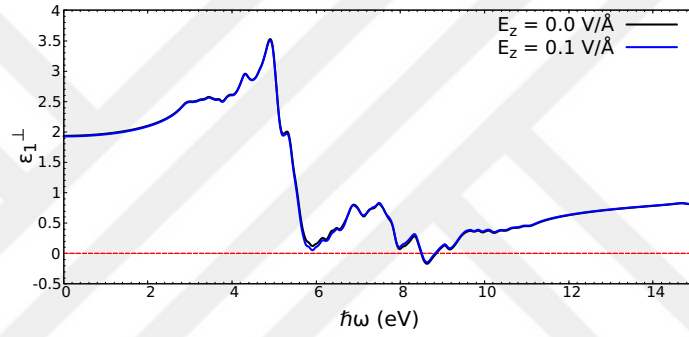


(d)

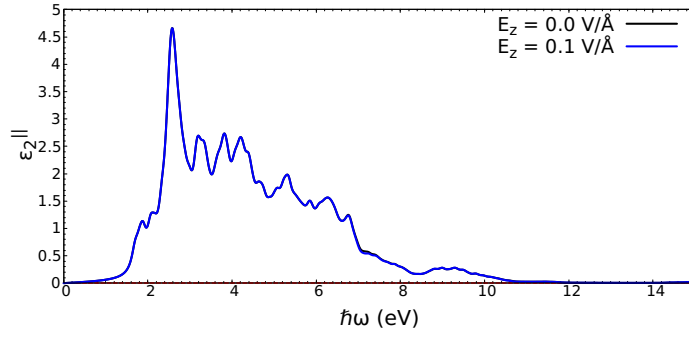
Figure 5.35: For monolayer tungsten diselenide without any external field effects: (a) $\varepsilon_1^{\parallel}$ plot. (b) $\varepsilon_1^{\perp}$ plot. (c) $\varepsilon_2^{\parallel}$ plot. (d) $\varepsilon_2^{\perp}$ plot.



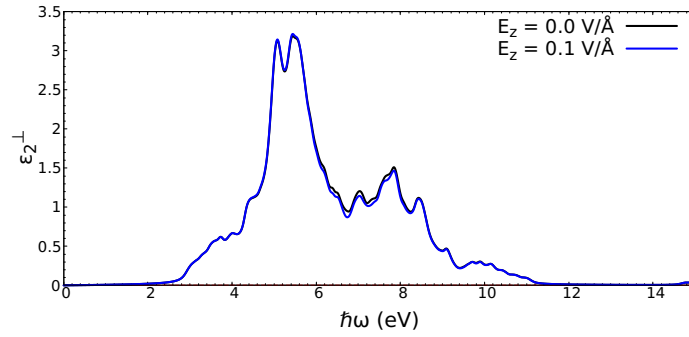
(a)



(b)

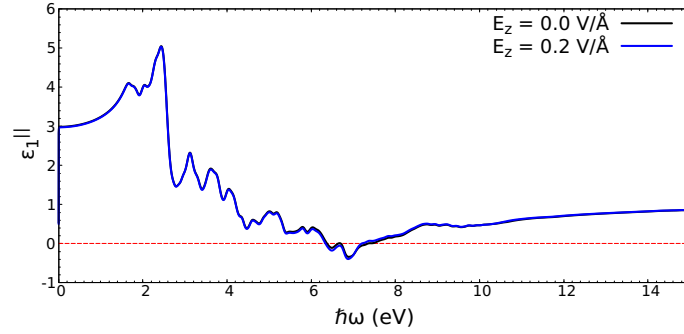


(c)

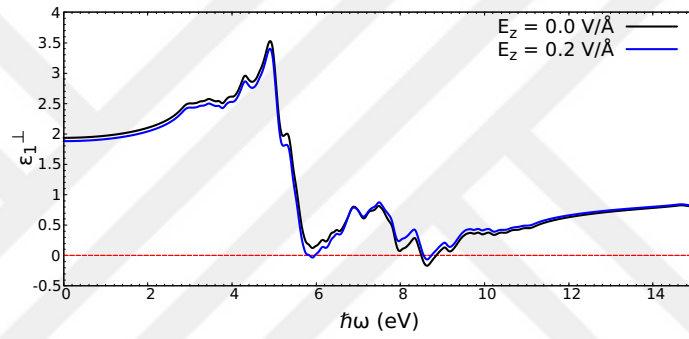


(d)

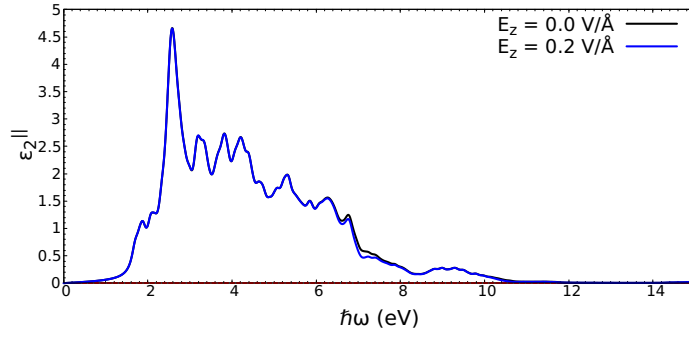
Figure 5.36: Dielectric function data in the presence of an E-field of magnitude $E_z=0.1$ V/Å: (a) $\epsilon_1^{\parallel}$ plot. (b) $\epsilon_1^{\perp}$ plot. (c) $\epsilon_2^{\parallel}$ plot. (d) $\epsilon_2^{\perp}$ plot.



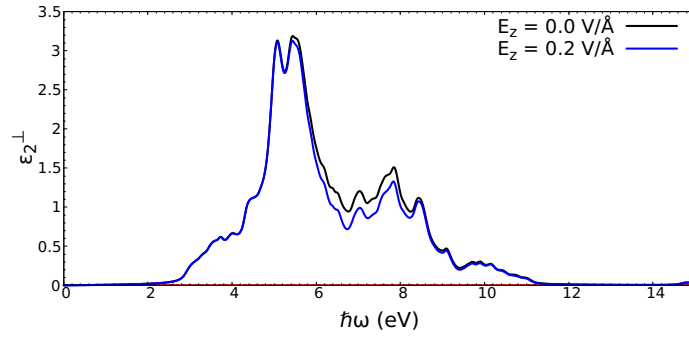
(a)



(b)

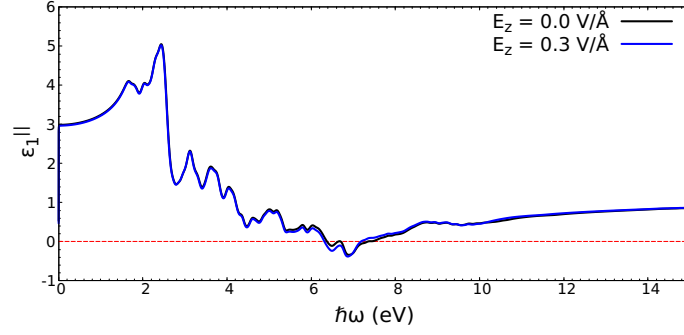


(c)

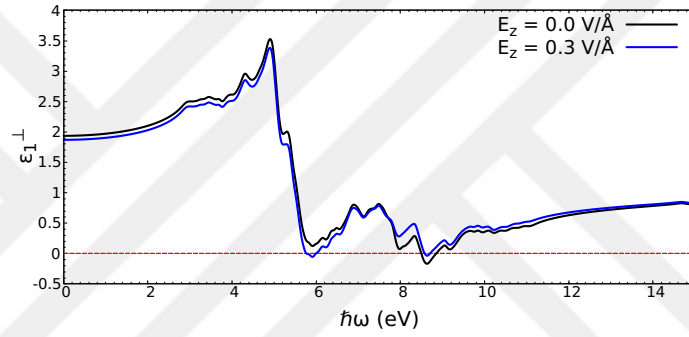


(d)

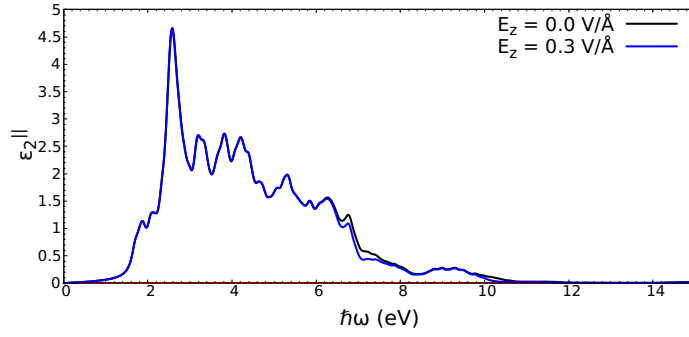
Figure 5.37: Dielectric function data under an E-field of magnitude $E_z=0.2 \text{ V/\AA}$:
(a) $\varepsilon_1^{\parallel}$ plot. (b) $\varepsilon_1^{\perp}$ plot. (c) $\varepsilon_2^{\parallel}$ plot. (d) $\varepsilon_2^{\perp}$ plot.



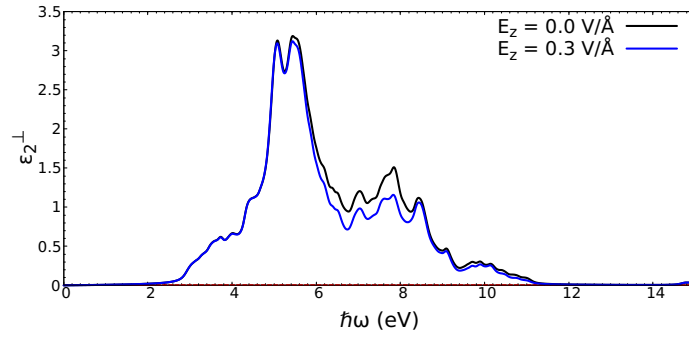
(a)



(b)

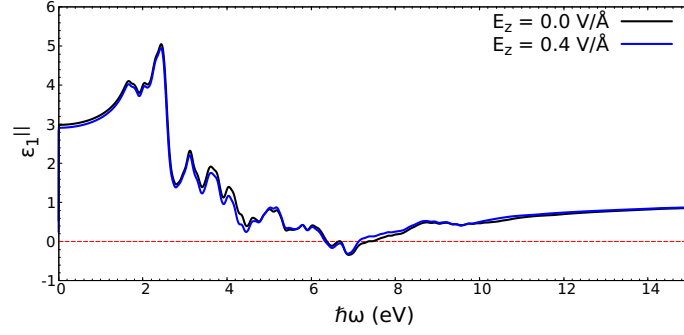


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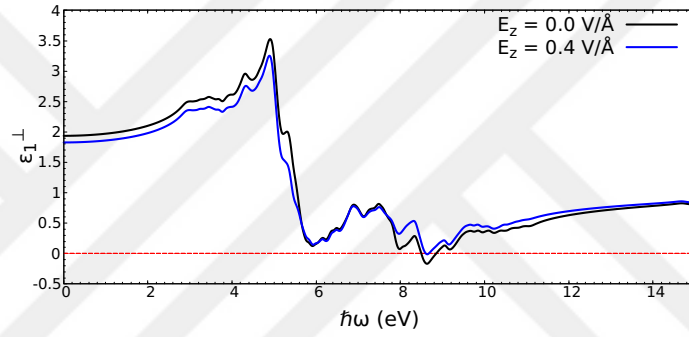


(d)

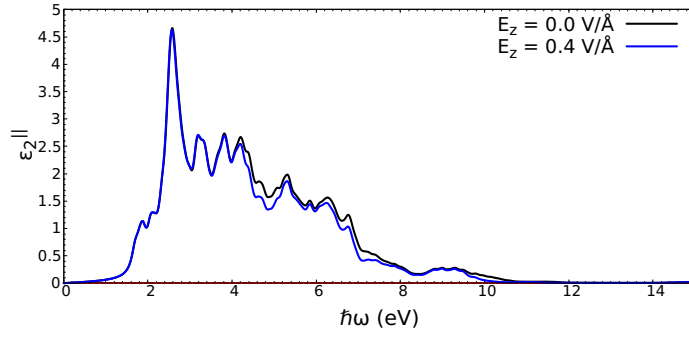
Figure 5.38: Dielectric function data under an E-field of magnitude $E_z=0.3 \text{ V/\AA}$:
(a) $\varepsilon_1^{\parallel}$ plot. (b) $\varepsilon_1^{\perp}$ plot. (c) $\varepsilon_2^{\parallel}$ plot. (d) $\varepsilon_2^{\perp}$ plot.



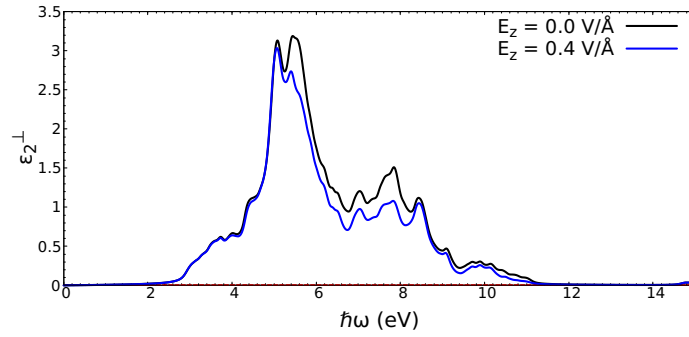
(a)



(b)

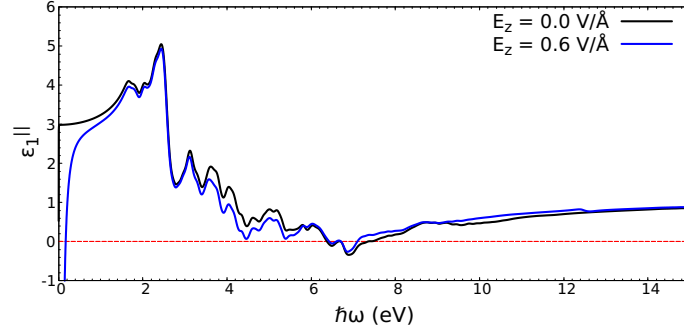


(c)

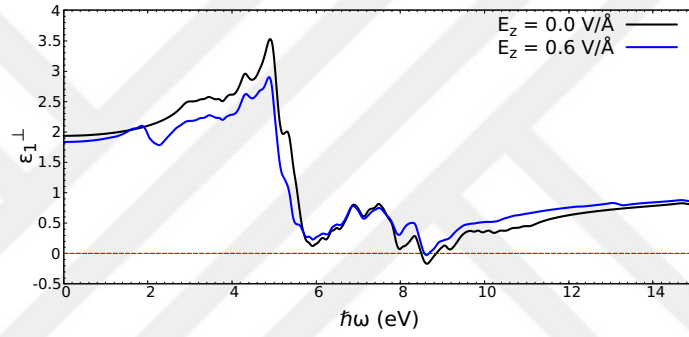


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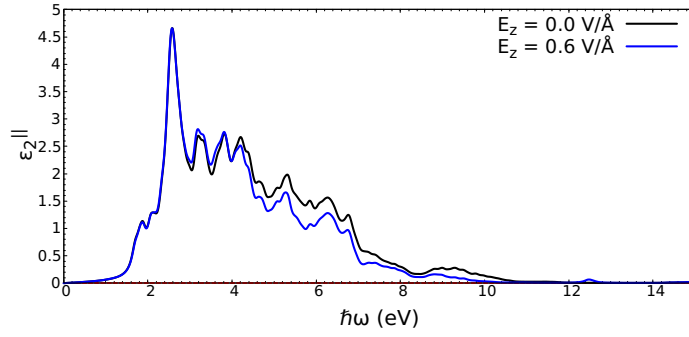
Figure 5.39: Dielectric function data under an E-field strength of $E_z=0.4$ V/Å: (a) $\varepsilon_1^{\parallel}$ plot. (b) $\varepsilon_1^{\perp}$ plot. (c) $\varepsilon_2^{\parallel}$ plot. (d) $\varepsilon_2^{\perp}$ plot.



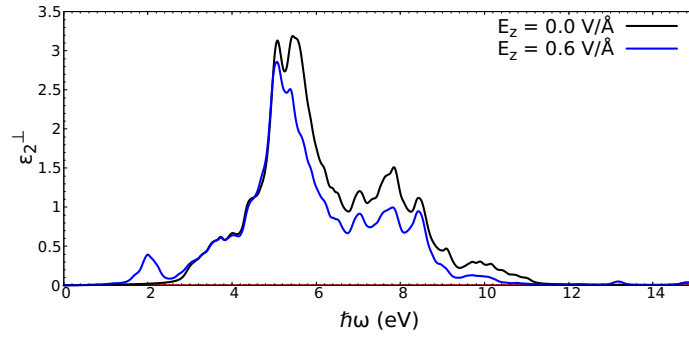
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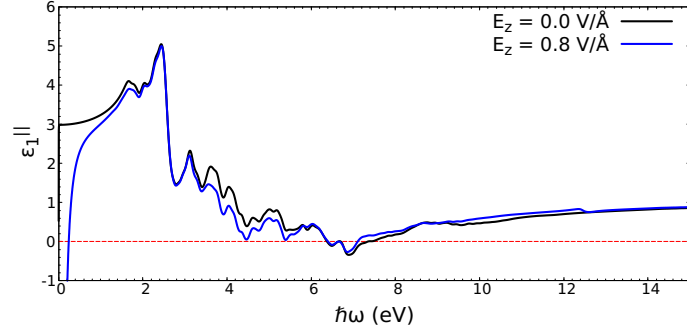


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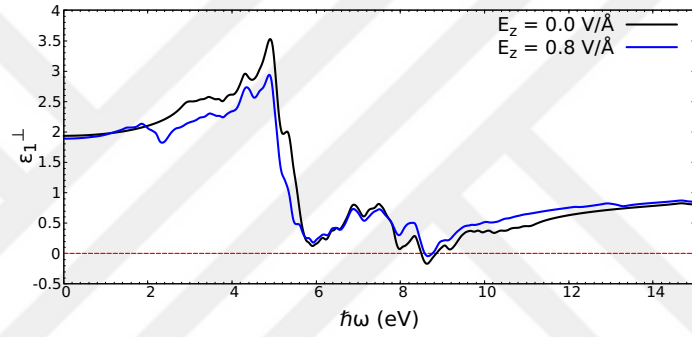


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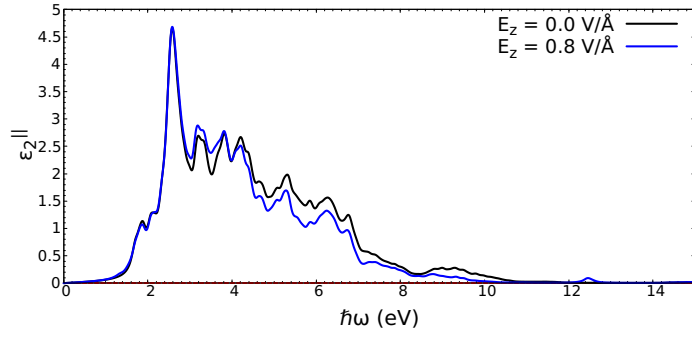
Figure 5.40: Dielectric function data in the presence of an E-field of magnitude $E_z=0.6$ V/Å: (a) $\epsilon_1^{\parallel}$ plot. (b) $\epsilon_1^{\perp}$ plot. (c) $\epsilon_2^{\parallel}$ plot. (d) $\epsilon_2^{\perp}$ plot.



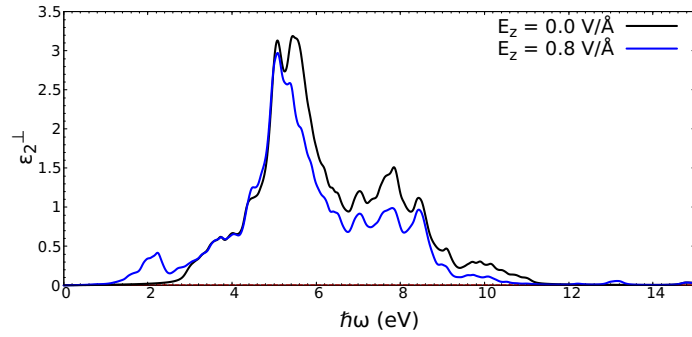
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(b)

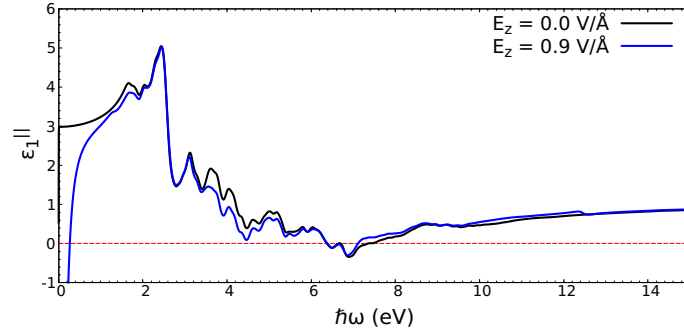


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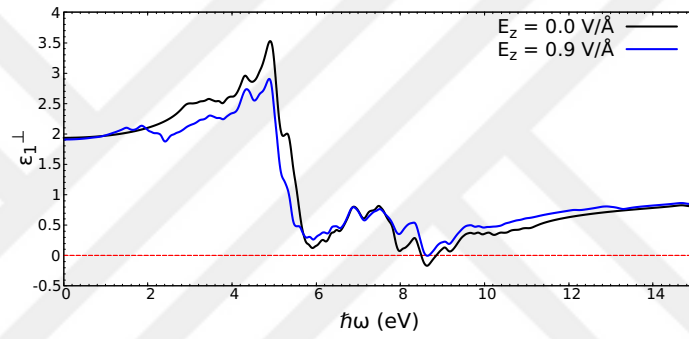


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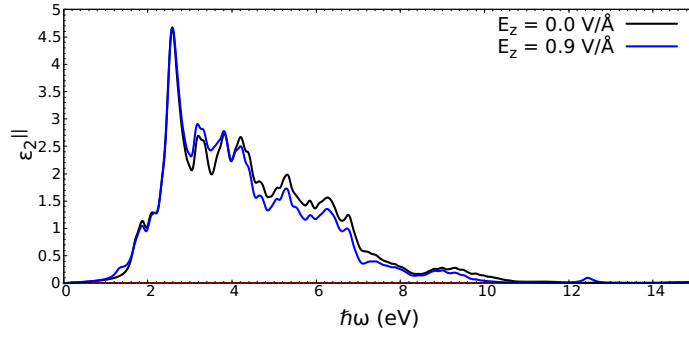
Figure 5.41: Dielectric function data under the influence of an E-field of magnitude $E_z=0.8$ V/Å: (a) $\varepsilon_1^{\parallel}$ plot. (b) $\varepsilon_1^{\perp}$ plot. (c) $\varepsilon_2^{\parallel}$ plot. (d) $\varepsilon_2^{\perp}$ plot.



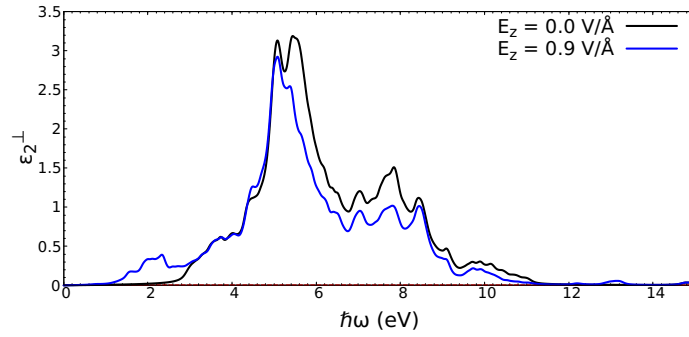
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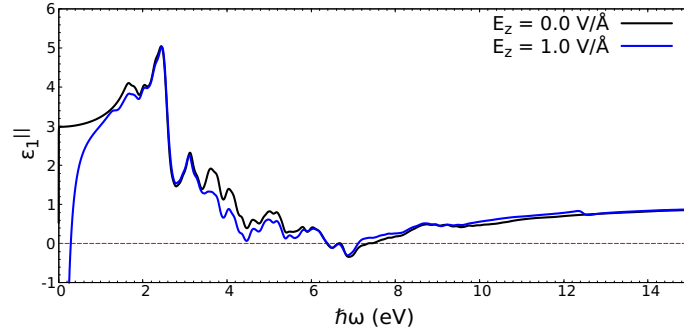


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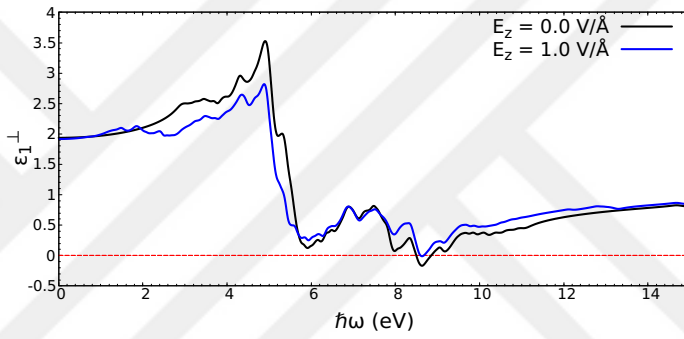


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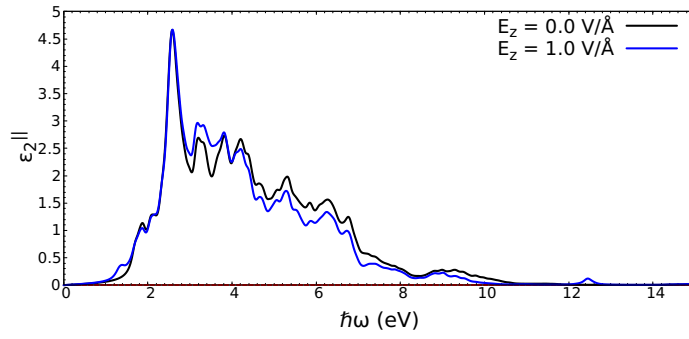
Figure 5.42: Dielectric function data under an E-field of magnitude $E_z=0.9$ V/Å: (a) $\epsilon_1^{\parallel}$ plot. (b) $\epsilon_1^{\perp}$ plot. (c) $\epsilon_2^{\parallel}$ plot. (d) $\epsilon_2^{\perp}$ plot.



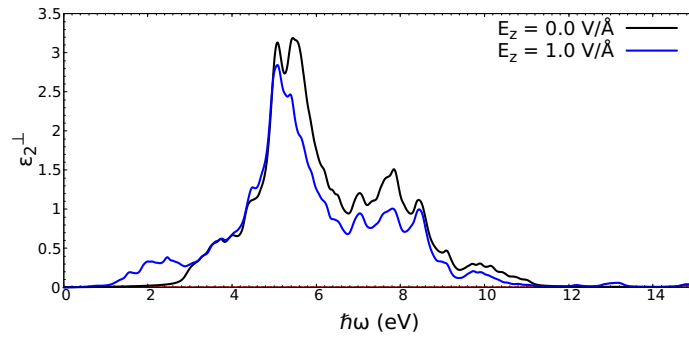
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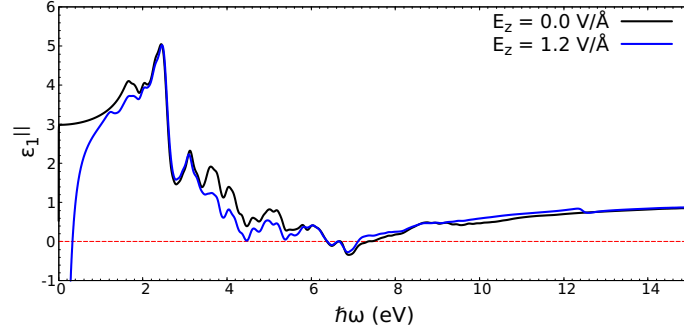


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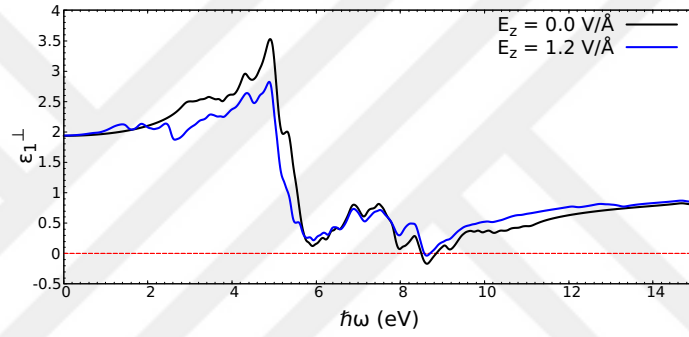


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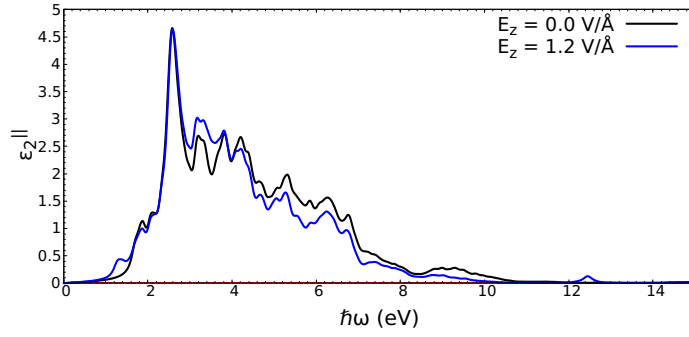
Figure 5.43: Dielectric function data under an E-field of magnitude $E_z=1.0 \text{ V/\AA}$: (a) $\epsilon_1^{\parallel}$ plot. (b) $\epsilon_1^{\perp}$ plot. (c) $\epsilon_2^{\parallel}$ plot. (d) $\epsilon_2^{\perp}$ plot.



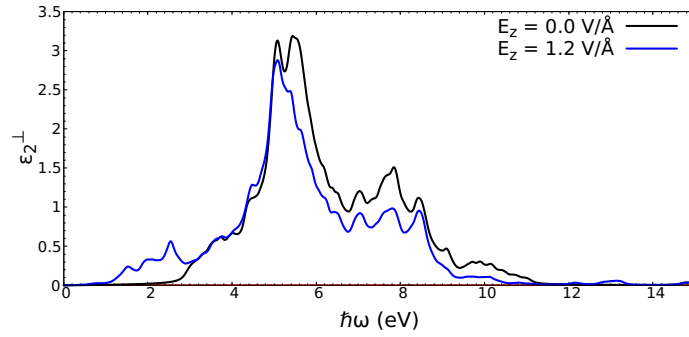
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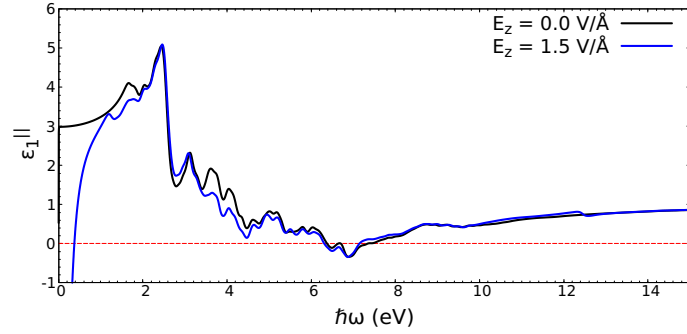


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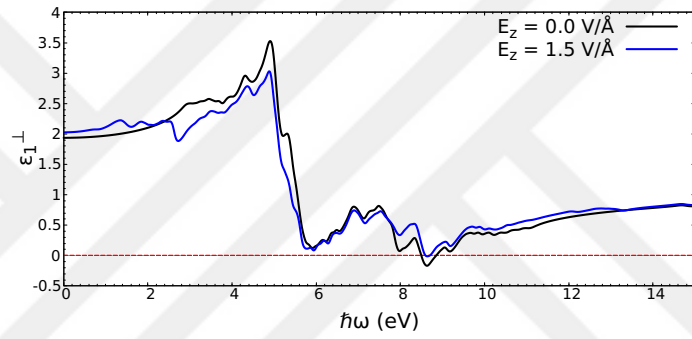


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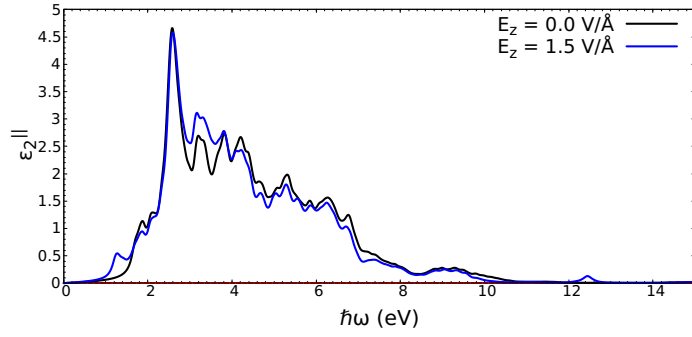
Figure 5.44: Dielectric function data in the presence of an E-field of magnitude $E_z=1.2$ V/Å: (a) $\epsilon_1^{\parallel}$ plot. (b) $\epsilon_1^{\perp}$ plot. (c) $\epsilon_2^{\parallel}$ plot. (d) $\epsilon_2^{\perp}$ plot.



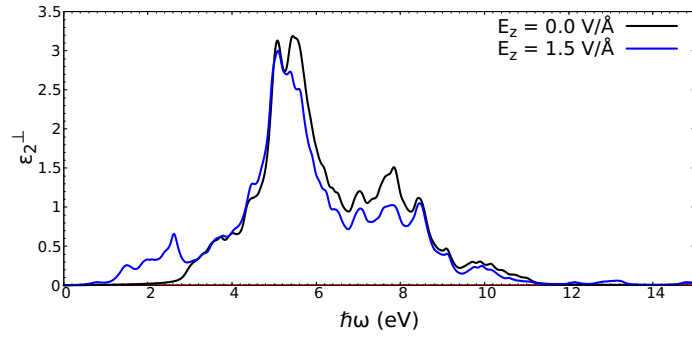
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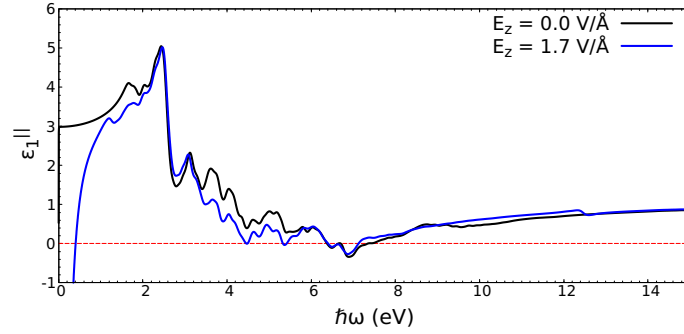


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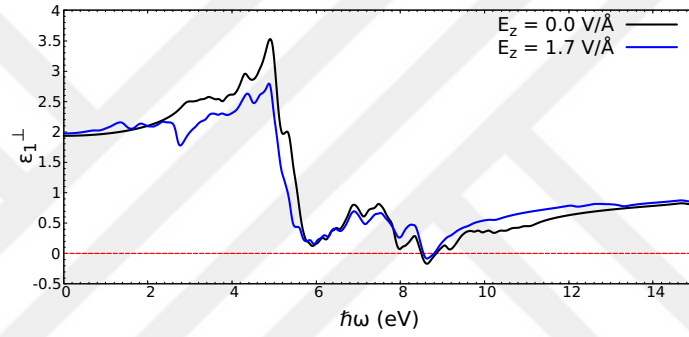


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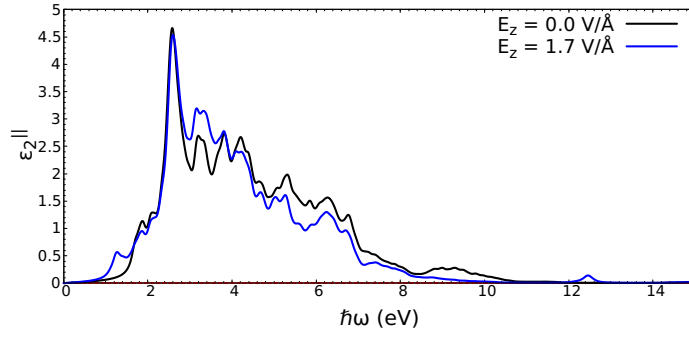
Figure 5.45: Dielectric function data under the influence of an E-field of magnitude $E_z=1.5$ V/Å: (a) $\varepsilon_1^{\parallel}$ plot. (b) $\varepsilon_1^{\perp}$ plot. (c) $\varepsilon_2^{\parallel}$ plot. (d) $\varepsilon_2^{\perp}$ plot.



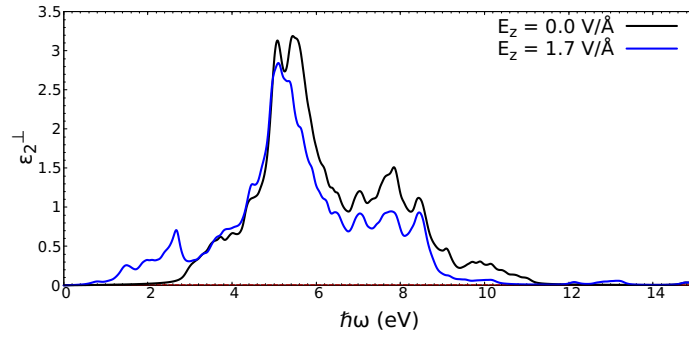
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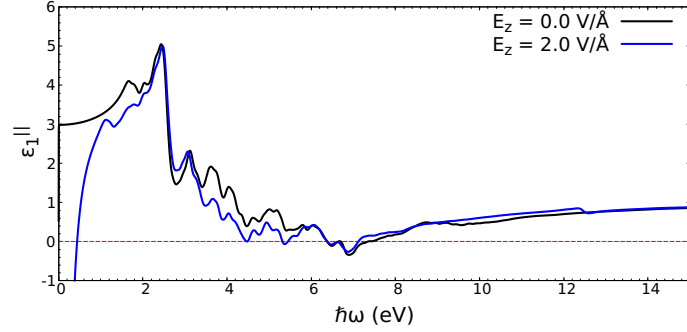


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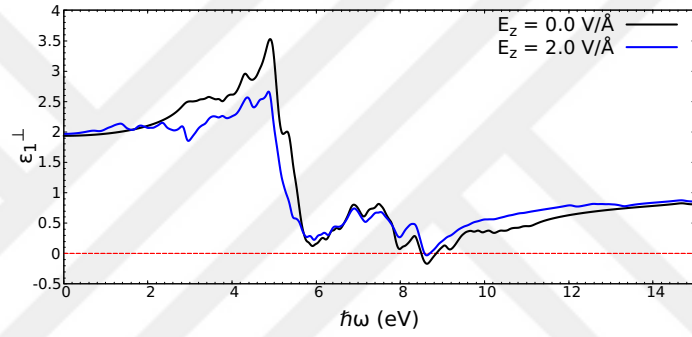


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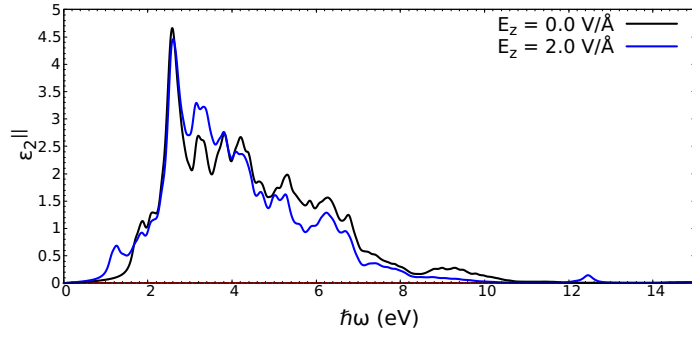
Figure 5.46: Dielectric function data when the magnitude of the perpendicularly applied E-field is $E_z=1.7$ V/Å: (a) $\varepsilon_1^{\parallel}$ plot. (b) $\varepsilon_1^{\perp}$ plot. (c) $\varepsilon_2^{\parallel}$ plot. (d) $\varepsilon_2^{\perp}$ plot.



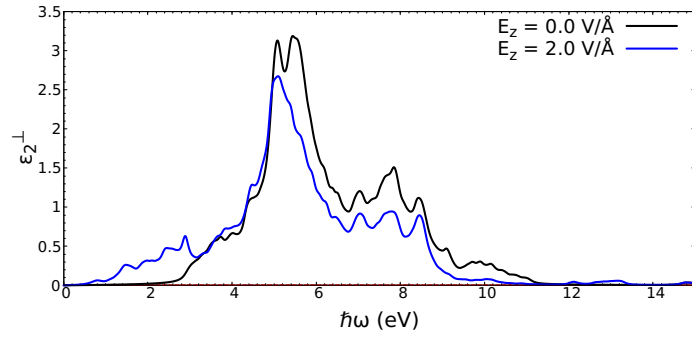
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(b)

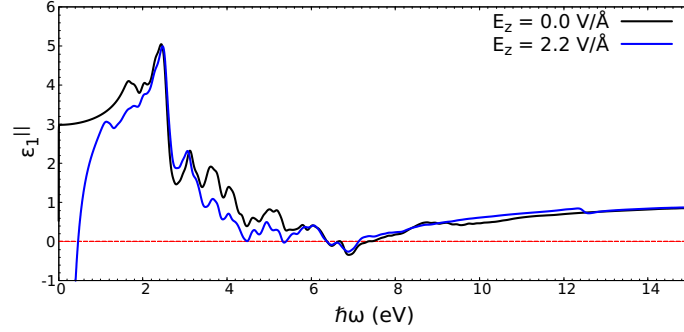


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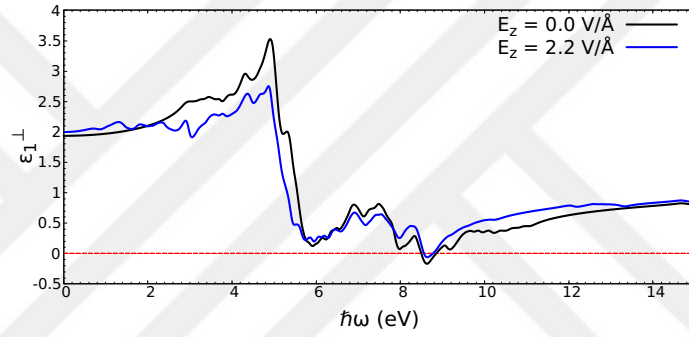


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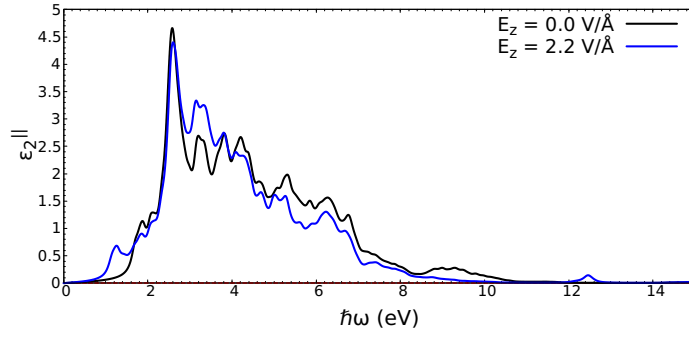
Figure 5.47: Dielectric function data in the presence of an E-field of magnitude $E_z=2.0$ V/Å: (a) $\epsilon_1^{\parallel}$ plot. (b) $\epsilon_1^{\perp}$ plot. (c) $\epsilon_2^{\parallel}$ plot. (d) $\epsilon_2^{\perp}$ plot.



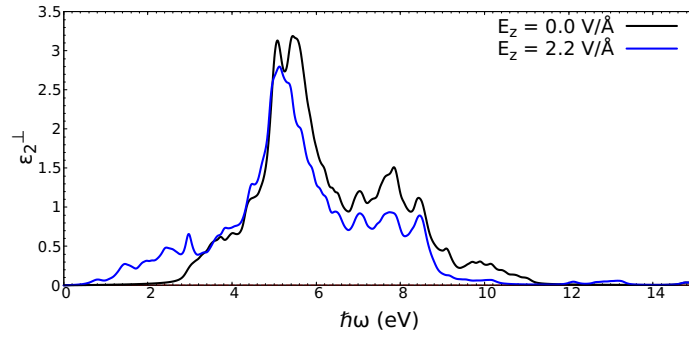
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(b)

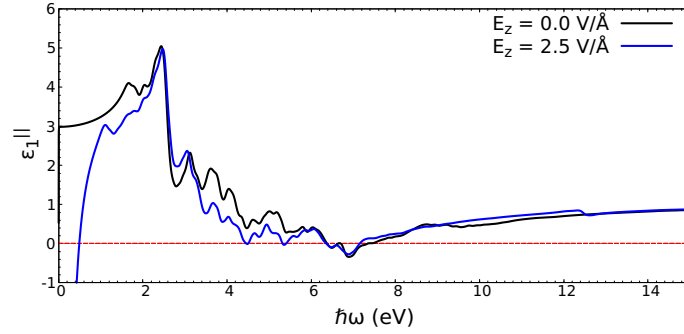


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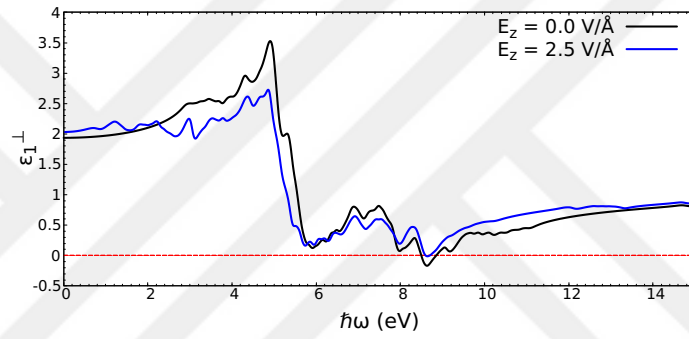


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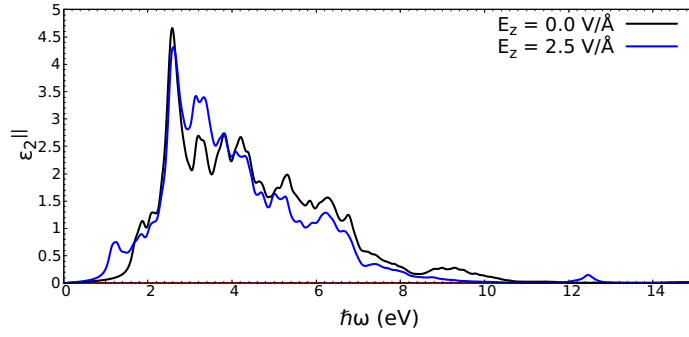
Figure 5.48: Dielectric function data under a perpendicular E-field of magnitude $E_z=2.2$ V/Å: (a) $\epsilon_1^{\parallel}$ plot. (b) $\epsilon_1^{\perp}$ plot. (c) $\epsilon_2^{\parallel}$ plot. (d) $\epsilon_2^{\perp}$ plot.



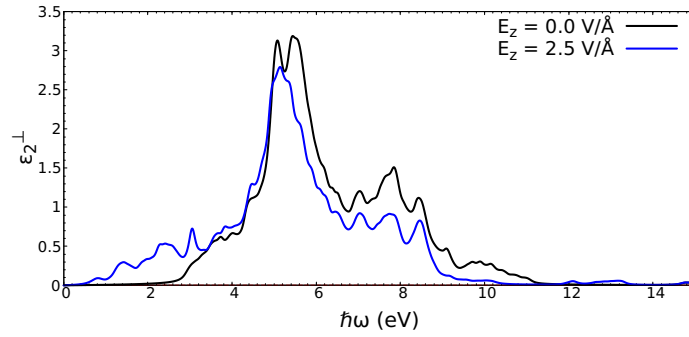
(a)



(b)



(c)



(d)

Figure 5.49: Dielectric function data when the magnitude of the perpendicularly applied E-field is $E_z=2.5$ V/Å: (a) $\epsilon_1^{\parallel}$ plot. (b) $\epsilon_1^{\perp}$ plot. (c) $\epsilon_2^{\parallel}$ plot. (d) $\epsilon_2^{\perp}$ plot.

Table 5.4 tabulates data of plasmon frequencies along x, y, and z directions indicated as PP_x , PP_y , and PP_z , respectively under the vertical static electric field.

E_z (V/Å)	PP_x (eV)	PP_y (eV)	PP_z (eV)
0.0	5.69	5.69	5.79
0.1	5.77	5.77	5.77
0.2	5.72	5.72	5.58
0.3	5.66	5.66	5.51
0.4	5.52	5.52	5.36
0.6	5.32	5.32	5.06
0.8	5.38	5.38	5.15
0.9	5.48	5.48	5.25
1.0	5.48	5.48	5.22
1.2	5.42	5.41	5.17
1.5	5.64	5.64	5.48
1.7	5.38	5.38	5.14
2.0	5.39	5.39	5.09
2.2	5.40	5.40	5.15
2.5	5.41	5.41	5.14

Table 5.4: Position of plasmon peaks with changing E-field magnitudes.

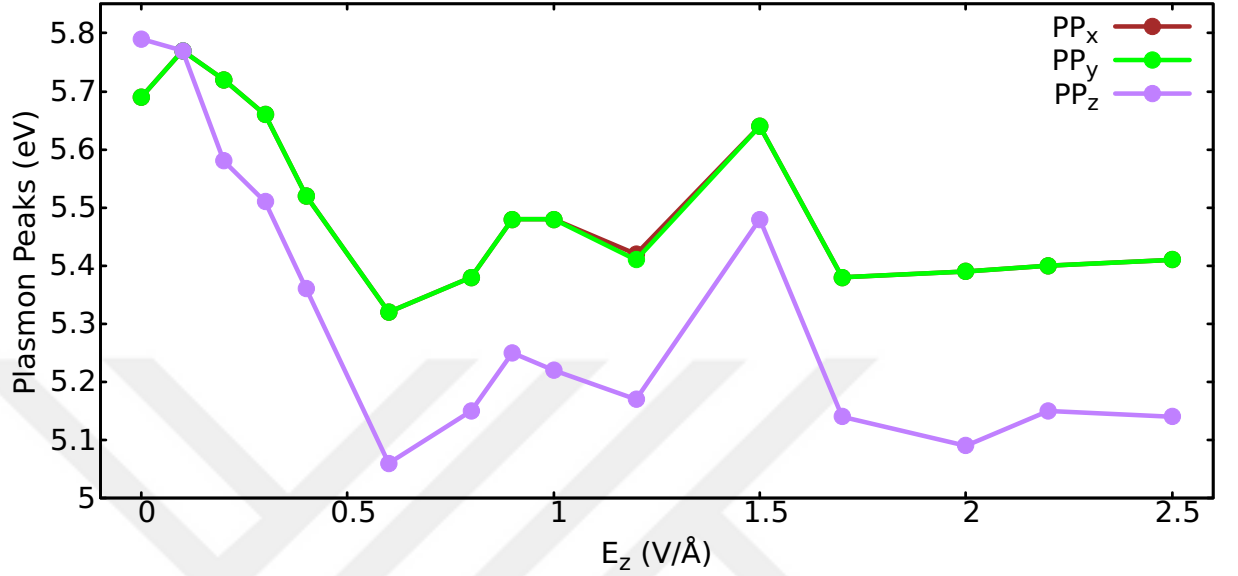


Figure 5.50: Change of PP_x , PP_y , and PP_z under the vertical electric field.

Plot in Fig. 5.50 is the visual version of Table 5.4. As can be seen with ease, plasmon peaks along the x and y directions coincide whereas PP_z differs from them. However, curves follow almost the same behavior, in general. Up to 0.6 V/Å , plasmon peaks along the z-axis redshifted. Plasmon peaks along x- and y-directions also redshifted between 0.1 V/Å and 0.6 V/Å whereas they started to blueshift for $E_z \geq 1.7 \text{ V/Å}$. When the field strength is between 0.6 V/Å and 0.8 V/Å , PP_z blueshifted. PP_z changed between 5.8 eV and 5.1 eV whereas PP_x and PP_y fluctuated between 5.8 eV and 5.4 eV under the vertical E-field.

When the strength of the E-field is 0.1 V/Å , no significant changes are observed for all components of ε_1 and ε_2 . At 0.2 V/Å , the dip around 5.9 eV $\varepsilon_1^\perp$ shifted below zero. Between 5.6 eV and 8.6 eV , the amplitude of $\varepsilon_2^\perp$ curve decreased.

For $E_z = 0.3 \text{ V/Å}$, between 5.4 eV and 7.0 eV , the amplitude of $\varepsilon_1^\parallel$ curve barely decreased whereas it increased between 7.0 eV and 8.0 eV . Between 0.0 eV and 7.0 eV , the amplitude of $\varepsilon_1^\perp$ curve decreased whereas it increased after 7.0 eV which is also observed for 0.4 V/Å . The peak around 7 eV decreased in $\varepsilon_2^\parallel$ data as well. After 5.4 eV , amplitude of $\varepsilon_2^\perp$ curve decreased.

When $E_z = 0.4 \text{ V/\AA}$, between 0.0-4.6 eV, amplitude of $\epsilon_1^{\parallel}$ got lower whereas it increased after 7 eV. Between 4-11 eV decrease in ϵ_2 data continued. Additionally, after $0.3 \text{ V/\AA}$, in $\epsilon_2^{\perp}$ plot the peak around 5.6 eV started redshifting up to $2.5 \text{ V/\AA}$.

At $E_z = 0.6 \text{ V/\AA}$, between 0-0.2 eV, $\epsilon_1^{\parallel}$ decreased drastically and this behavior remained such (and the interval of it is reached towards 0.4 eV) up to $2.5 \text{ V/\AA}$. A significant change occurred in that electric field amplitude is the new peak appeared at 2 eV in $\epsilon_1^{\perp}$ and $\epsilon_2^{\perp}$ plots which indicates a transition of 2 eV. Moreover, the last mentioned peak in $\epsilon_2^{\perp}$ data blueshifted, the peak became wider, and its amplitude strengthened as the amplitude of the E-field increased. Moreover, in $\epsilon_2^{\parallel}$ plot, the peak around 3.2 eV started to have greater amplitude and it gained strength by increasing E-field amplitudes.

After $0.8 \text{ V/\AA}$, the amplitude of the peak around 4.5 eV in $\epsilon_2^{\perp}$ plot is increased and kept increasing as the E-field amplitude increased.

Starting from $E_z = 0.9 \text{ V/\AA}$, a new peak appeared around 1.3 eV in $\epsilon_2^{\parallel}$ plot and it became more obvious as the E-field got stronger. Around 12.5 eV another peak is observed in ϵ_2 plots and its amplitude slightly increased up to $2.5 \text{ V/\AA}$ in $\epsilon_2^{\perp}$ plot.

To sum up, under the vertical static electric field on 2D tungsten selenide, the most significant changes occurring in the dielectric function spectra based on DFT is the broad peaks appearing in the low energy zone (between 0 eV and 5 eV) which are started from $0.6 \text{ V/\AA}$. Notice that the band gap of this system decreased drastically at $0.6 \text{ V/\AA}$ as illustrated in Fig. 5.33. $0.6 \text{ V/\AA}$ was also a critical value for electronic calculations in Chapter 5.1.1 since the degeneracy in the VB has broken at $E_z = 0.6 \text{ V/\AA}$. The most interesting change observed for 2D WSe_2 under the vertical electric field is the phase transition that took place at $E_z = 1.0 \text{ V/\AA}$ since the band gap became zero and bands in VB and CB overlapped.

Chapter 6

Conclusion

In this thesis, by the calculations based on the density functional theory, the electronic and optical properties of metallic and semiconducting 2D materials have been investigated in the presence of several magnitudes of the external static electric field that is applied perpendicular to the layer of those materials. As mentioned in the introduction, external effects such as an external electric field may change the properties of materials which is confirmed for three monolayers that are studied. External electric field changed the Fermi level for graphene, molybdenum carbide, and tungsten diselenide. By external electric field, band gap engineering is also possible and it is verified while investigating the electronic properties of monolayer WSe_2 . It has a band gap that is found as 1.649 eV (1.600 eV) using norm-conserving pseudo-potential (projector augmented wave pseudo-potential) by including the van der Waals interactions (VDW-DF2) since those interactions should be included for van der Waals materials for precision. For all studied systems, VDW-DF2 is used as XC functional.

In the case of single-layer graphene, degeneracy in the VB was broken when $E_z \geq 0.4$ V/Å. Additionally, π and π^* bands shifted upward direction as the magnitude of the E-field increased. When $E_z \geq 0.5$ V/Å, σ^* band shifted below the Fermi level, and by increasing E-field strength, σ^* shifted more which enabled us to n-dope this material under the vertical static electric field. Without any

external effects, the possible well-known interband transitions correspond to the monolayer graphene are $\pi \rightarrow \pi^*$ (around 3.8 eV) and $\sigma \rightarrow \sigma^*$ (at 14 eV) which are detected by $\varepsilon_2^{\parallel}$ data, and $\pi \rightarrow \sigma^*$ (at 10.38 eV) and $\sigma \rightarrow \pi^*$ (at 14.45 eV) transitions which can be investigated by $\varepsilon_2^{\perp}$ plot. Under the E-field, the positions of the peaks corresponding to $\pi \rightarrow \pi^*$ and $\sigma \rightarrow \sigma^*$ transitions did not change significantly. In addition to those four transitions as mentioned above, by the effect of E-field, a $\sigma^* \rightarrow \pi^*$ transition is observed which took place around Γ point in the first Brillouin zone towards the Dirac point. Moreover, by applying a vertical static electric field, detecting $\pi \rightarrow \pi^*$ and $\sigma \rightarrow \sigma^*$ transitions by making use of $\varepsilon_2^{\perp}$ plot became possible. In the $\varepsilon_2^{\perp}$ plots after 15 eV, a redshift is observed when the amplitude of the E-field is $0.1 \text{ V/\AA} \leq E_z \leq 0.2 \text{ V/\AA}$ whereas for $0.3 \text{ V/\AA} \leq E_z \leq 2.5 \text{ V/\AA}$ they blueshifted. Additionally between 10-15 eV of $\varepsilon_2^{\perp}$ plots, new peaks appeared around 12.5 eV and they strengthened as the E-field got stronger.

The second metallic monolayer that is investigated throughout the thesis is molybdenum carbide. Similarly, a degeneracy is observed in the VB that is broken when $E_z \geq 0.6 \text{ V/\AA}$. At $E_z = 0.8 \text{ V/\AA}$, the band corresponding to the s-orbital of Mo atoms shifted below the Fermi level which allows us to n-dope that system. Up to $E_z = 0.4 \text{ V/\AA}$ π plasmon peaks redshifted whereas blueshifted when $0.6 \text{ V/\AA} \leq E_z \leq 2.5 \text{ V/\AA}$.

Corresponding to 2D WSe_2 , degeneracy in the VB is broken at $E_z = 0.6 \text{ V/\AA}$, and also the band gap of this semiconductor considerably decreased at $0.6 \text{ V/\AA}$. Band gap of 2D WSe_2 disappeared under the E-field when $E_z = 1.0 \text{ V/\AA}$ and a phase transition from semiconductor to metal has been observed. Plasmon frequencies up to $0.6 \text{ V/\AA}$ in x, y, and z-directions redshifted. PP_x and PP_y fluctuated between 5.8 eV and 5.4 eV whereas PP_z changed between 5.8 eV and 5.1 eV in the presence of the static vertical electric field. In the $\varepsilon_1^{\perp}$ and $\varepsilon_2^{\perp}$ plots for single-layer WSe_2 , a new peak is observed at 2 eV and by increasing strengths of the E-field, that peak blueshifted, became wider and its amplitude strengthened. Additionally, starting with $E_z = 0.9 \text{ V/\AA}$, two peaks are observed at 1.3 eV (12.5 eV) in $\varepsilon_2^{\parallel}$ ($\varepsilon_2^{\perp}$) plot and strengthened with increasing E-field amplitudes. It is found that s-bands are quite sensitive to the vertical electric field.

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